Multifunctional Hybrid Composites for Thermal Materials

Task: 2302BL
Dr. Les Lee, Program Manager

03 August 2012
Arlington, VA

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Materials & Manufacturing Directorate
Air Force Research Laboratory

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Report Documentation Page						Form Approved OMB No. 0704-0188

1. REPORT DATE **03 AUG 2012**	2. REPORT TYPE	3. DATES COVERED **00-00-2012 to 00-00-2012**

4. TITLE AND SUBTITLE **Multifunctional Hybrid Composites for Thermal Materials**	5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Air Force Research Laboratory,Materials & Manufacturing Directorate,Wright Patterson AFB,OH,45433**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR’S ACRONYM(S) 11. SPONSOR/MONITOR’S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

Presented at the 2nd Multifunctional Materials for Defense Workshop in conjunction with the 2012 Annual Grantees’/Contractors’ Meeting for AFOSR Program on Mechanics of Multifunctional Materials & Microsystems Held 30 July - 3 August 2012 in Arlington, VA. Sponsored by AFRL, AFOSR, ARO, NRL, ONR, and ARL.

14. ABSTRACT

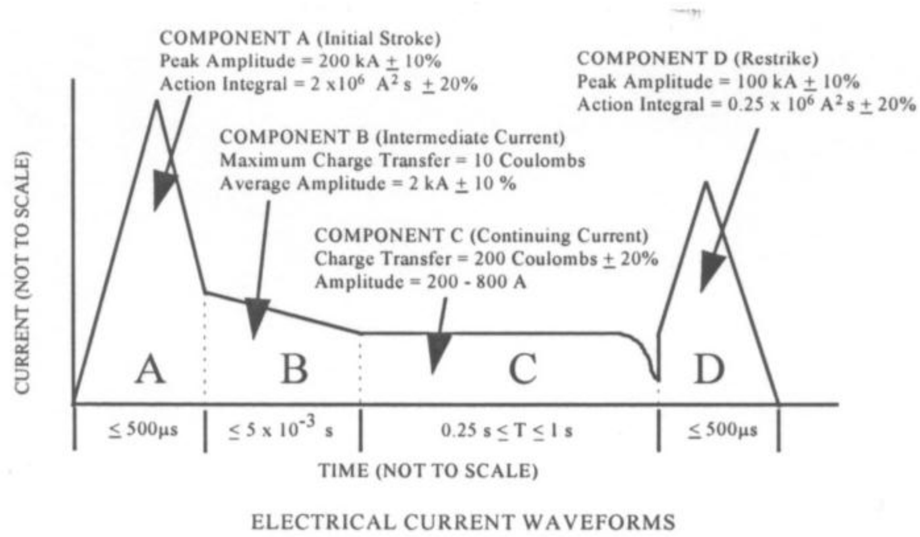
15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**35**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

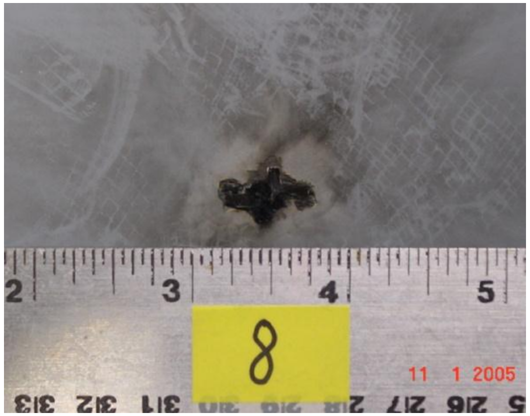
Why Conductive Composites?

- **Lightning strike related damage**
  - **Peak amplitude ~200 kA**
  - **Duration ~500μs**



Ref: MtL-STD-1757A

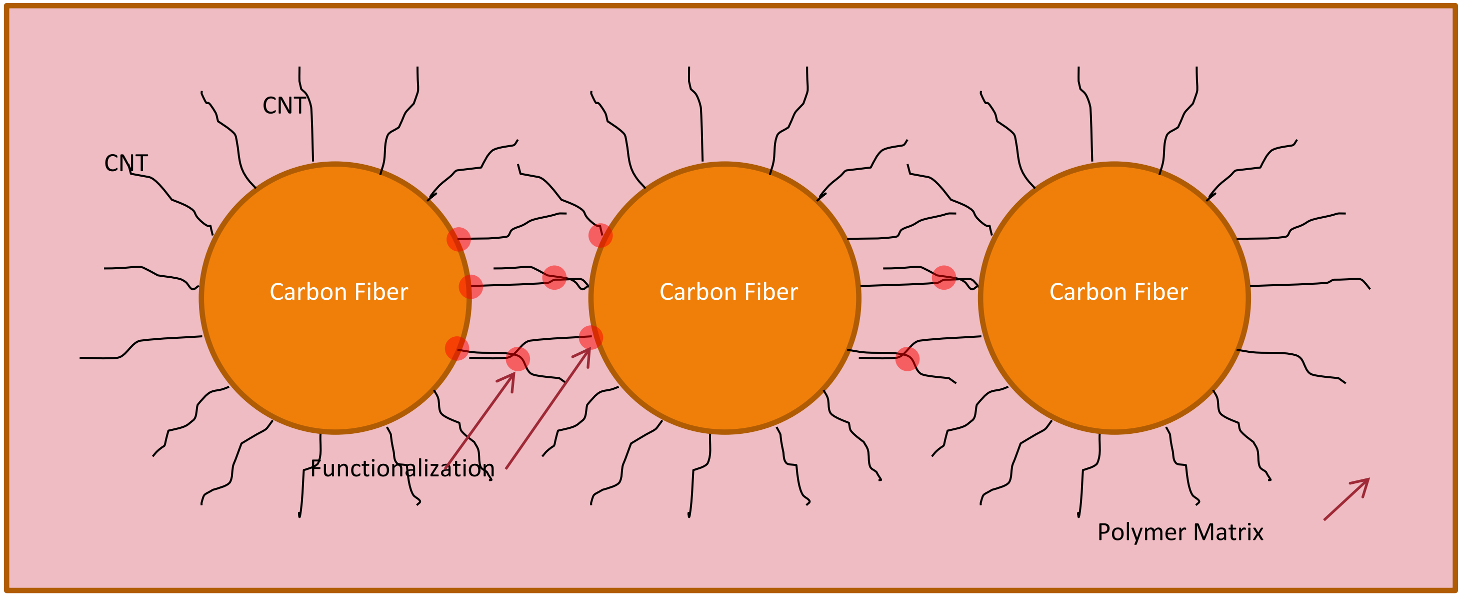
- **Protection against laser (DE weapons)**
  - **290 W/cm^2 shot chars paint and melts Al in 0.5 sec**



Ref: Fielding, et al, SAMPE, 2005

Overall Objective

- **Hierarchical carbon fiber morphology for tailored thermal properties in heterogeneous materials systems**
  - **Fiber reinforced composites**
  - **Sensors, Heat sink, etc.**



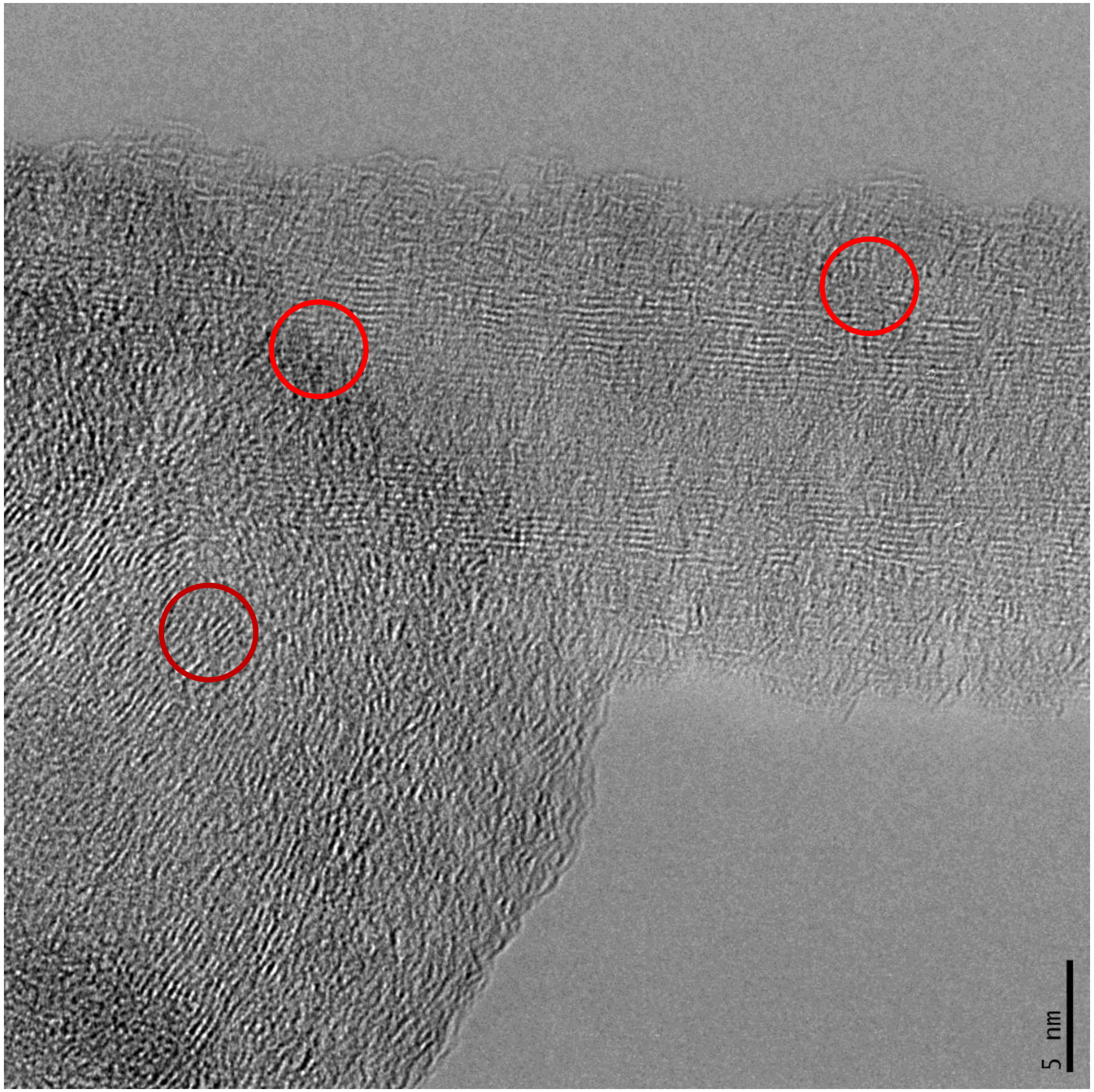
Achieving the appropriate thermal interface morphology is essential

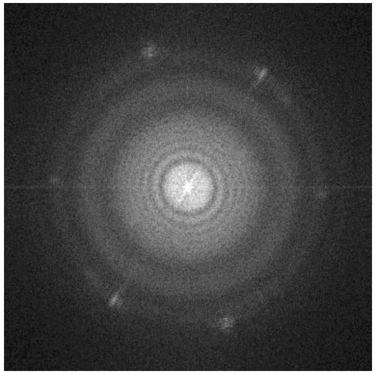
Interfaces: CNT-CNT; CNT-polymer; CNT-carbon fiber

Technical Progress
This year…

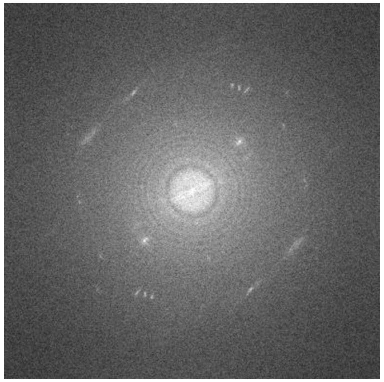
- **Wave Packets – single mode phonon transmission in functionalized CNT - J. Chem Physics, 135, 104109 (2011)**
- **Kapitza resistance – Boltzmann-Peierls-Callaway equation – a mesoscale computational tool - Physical Review E, 83, (2011)**
- **Thermal rectfication in asymmetric 3D nanostructure - Nano Letters, 2012**
- **Thermal conductivity reduction through helical nanowire superlattice structure (thermoelectrics) - Nanoscale, 2012, 4, 5009**
- **Thermal interface: a review - ACS Applied Mater. Interfaces, 4 (2), 2012**
- **Metal – CNT interface**
  - **MD simulation, processing, measurements**

MWCNT Graphite Interface (Hexagonal Crystal ED Patterns)

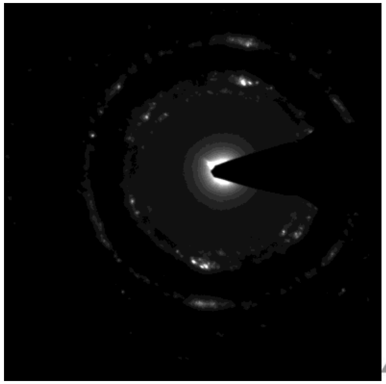




Nanotubes



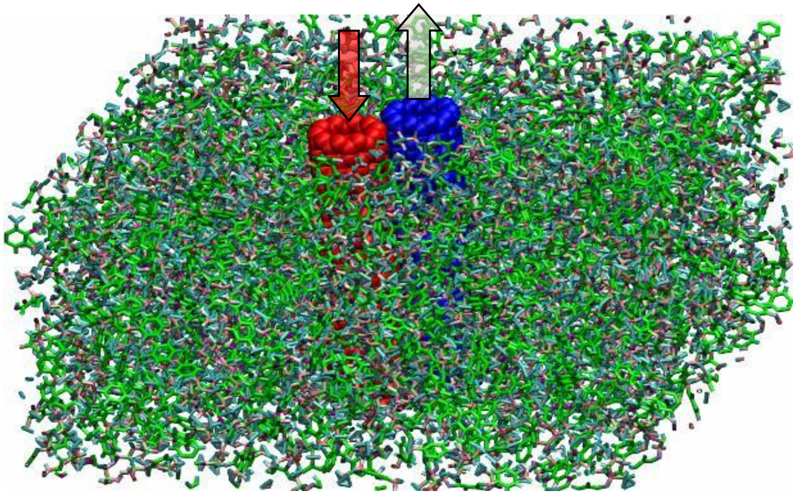
Substrate

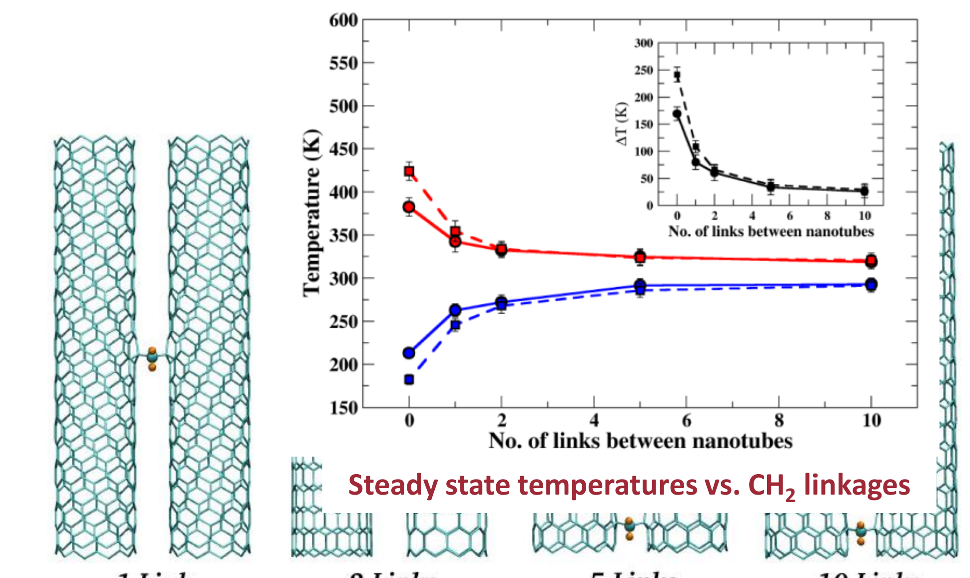


Interface

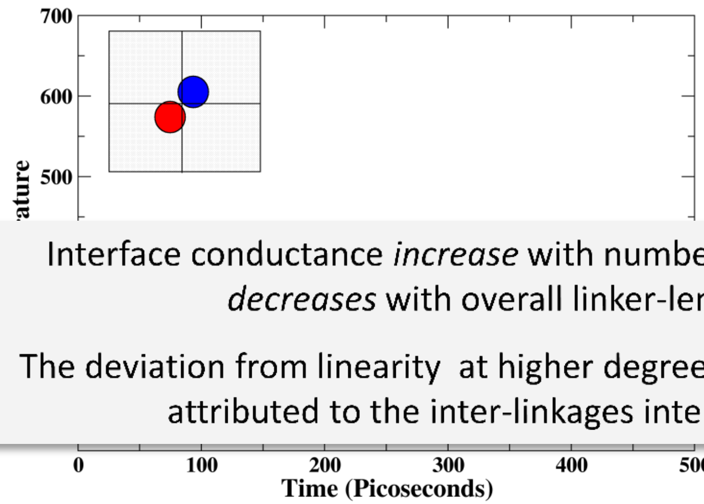
Interface Thermal Resistance across CNTs: Transverse Connection with Polymer Molecules

...





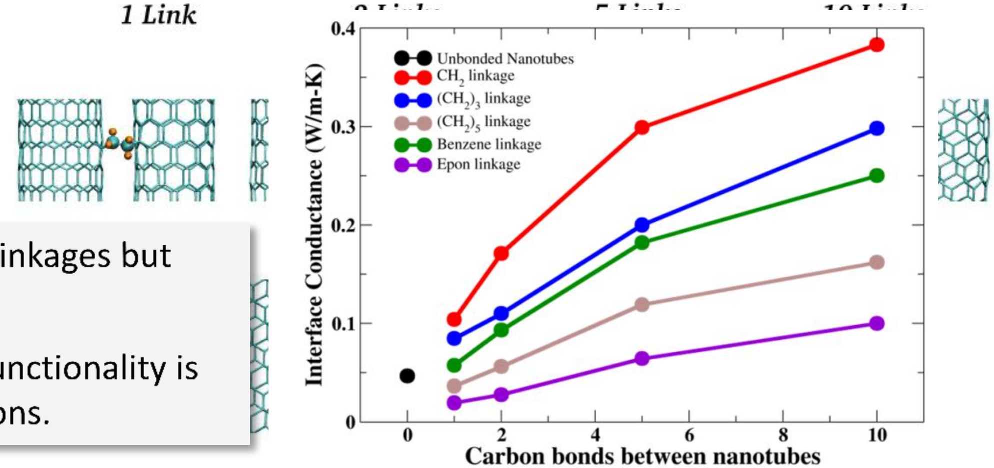
Steady state temperatures vs. CH_2 linkages



Temperature evolution

Interface conductance *increase* with number of linkages but *decreases* with overall linker-length.

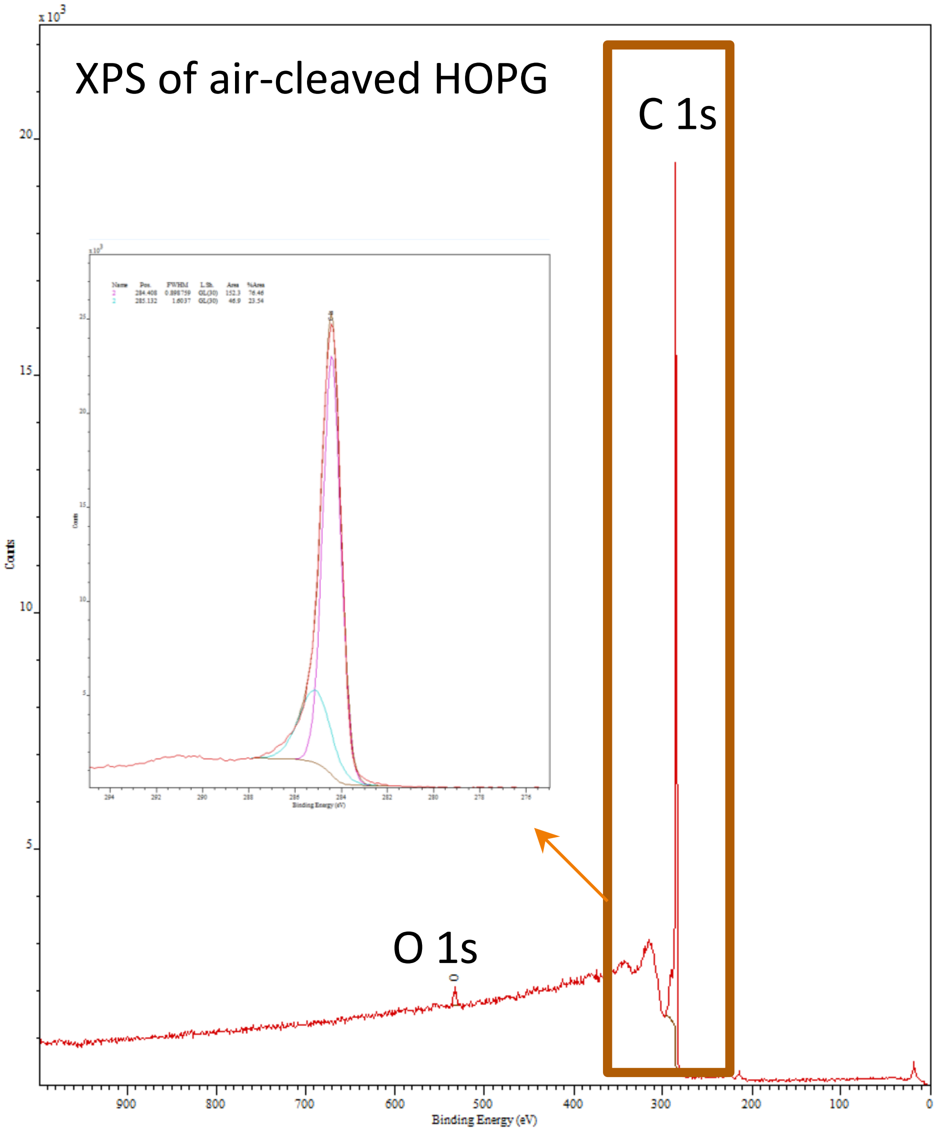
The deviation from linearity at higher degree of functionality is attributed to the inter-linkages interactions.

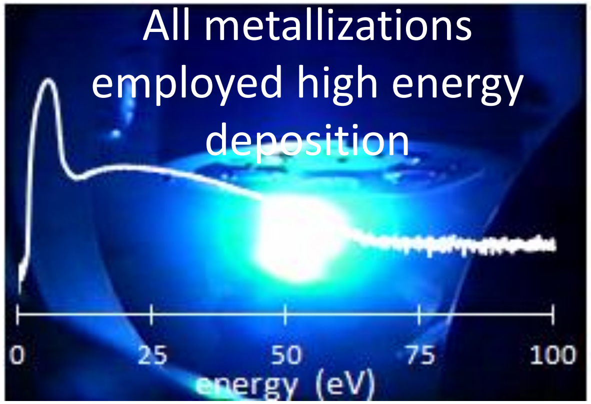


Effect of linkage length as well as their no. on overall interface conductance

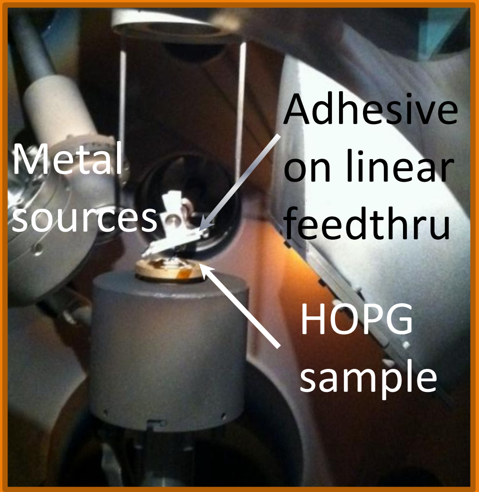
Varshney, *J. Phys. Chem. C* ***2010, 114***

Effects of Ambient Environment During Cleaving on Interfacial Chemistry



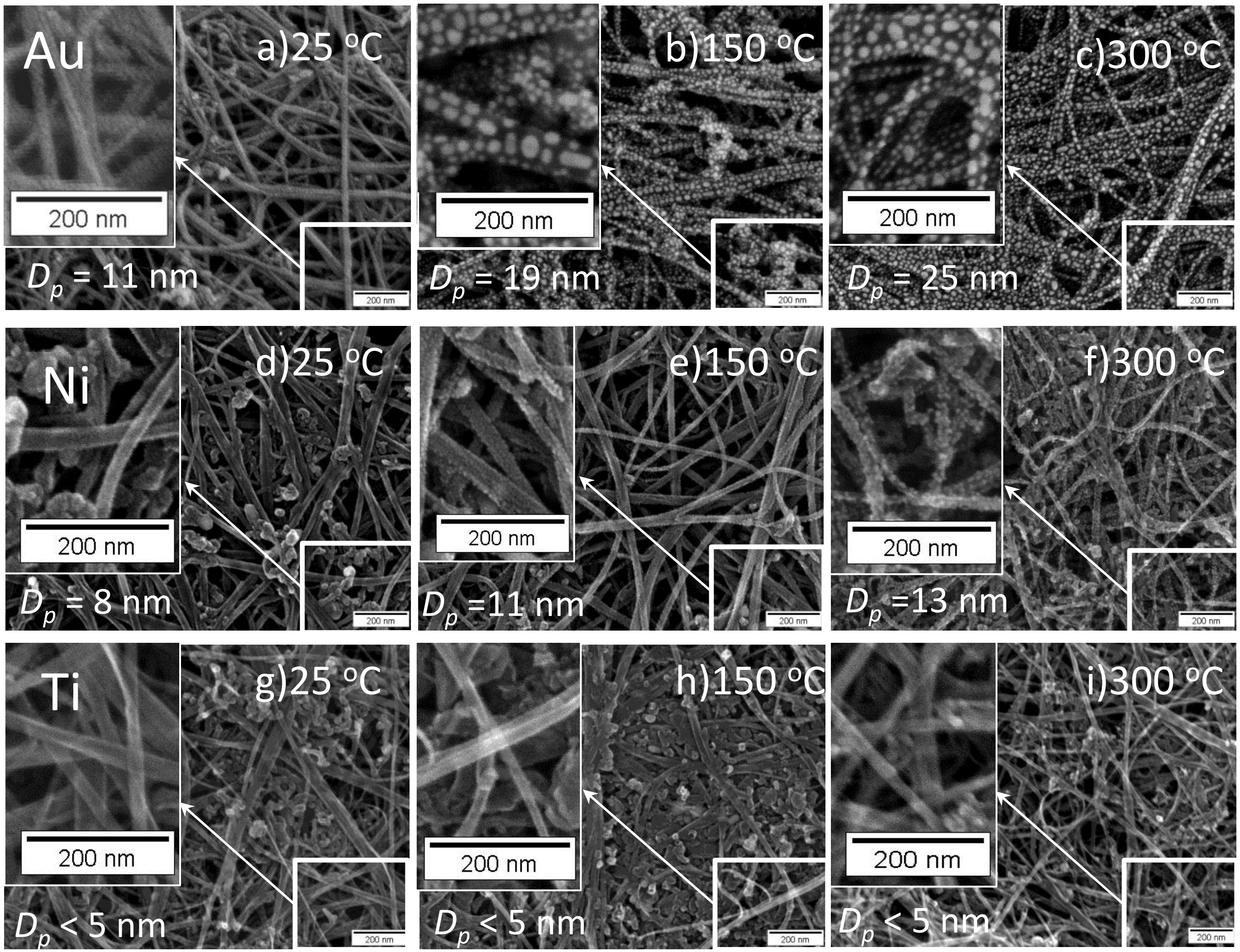


Vacuum cleaving apparatus



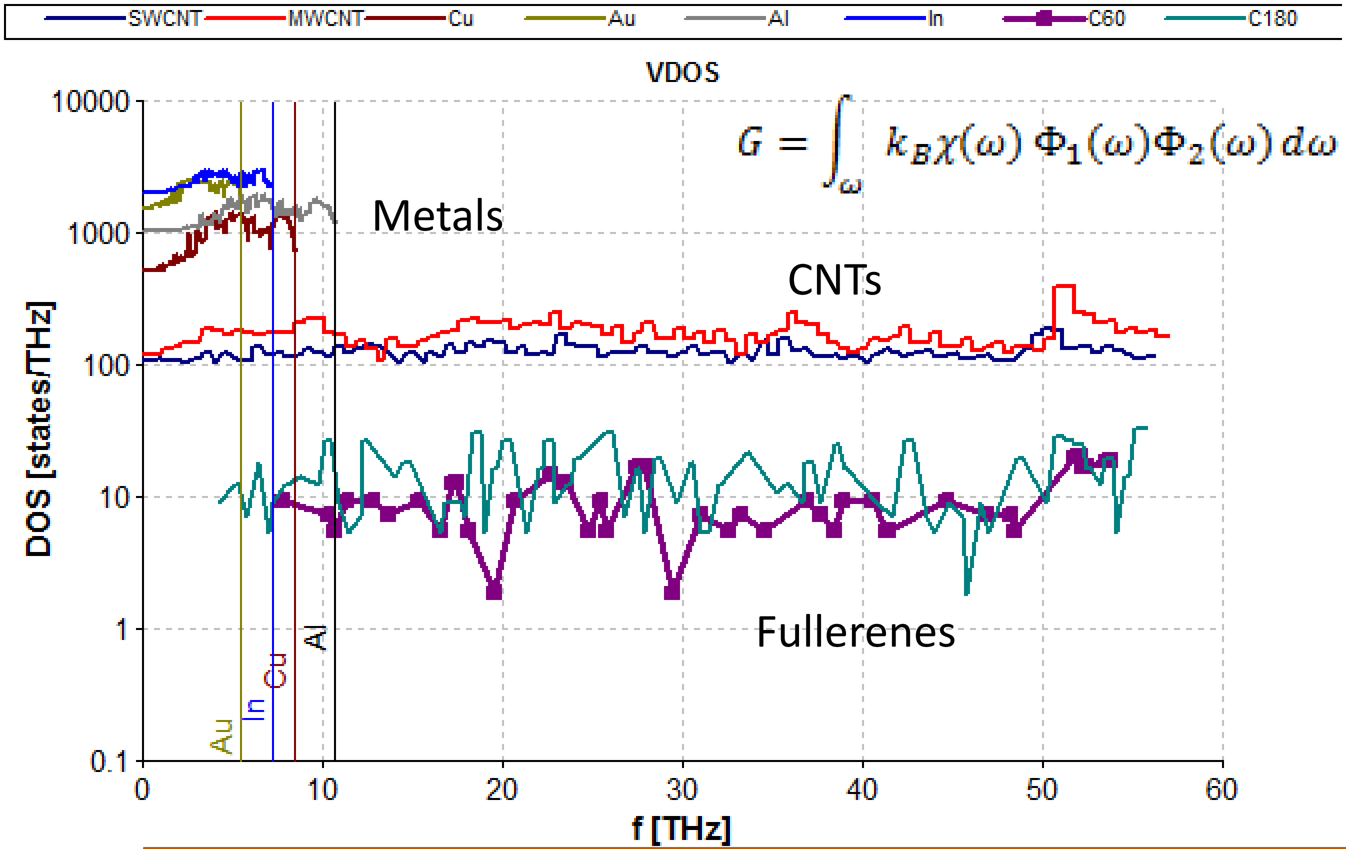
Intrinsic Factors Affecting Particle Morphology

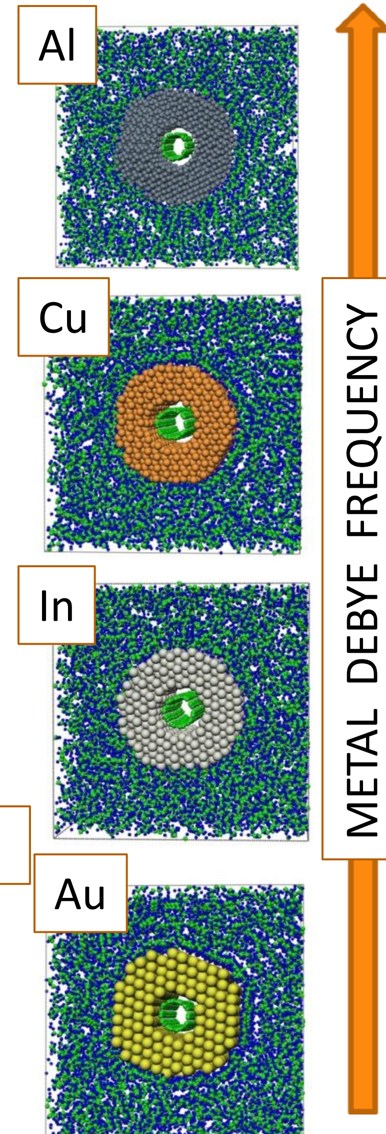
Increasing particle size



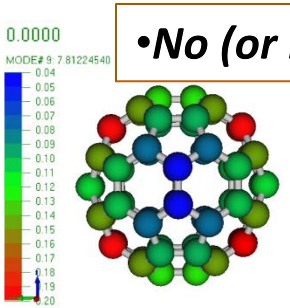
Increasing cohesive energy of metal

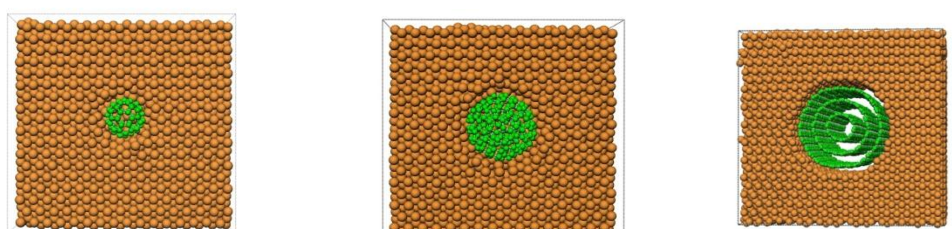
Simulation Approach: models of soft and hard carbon structures in metal matrix



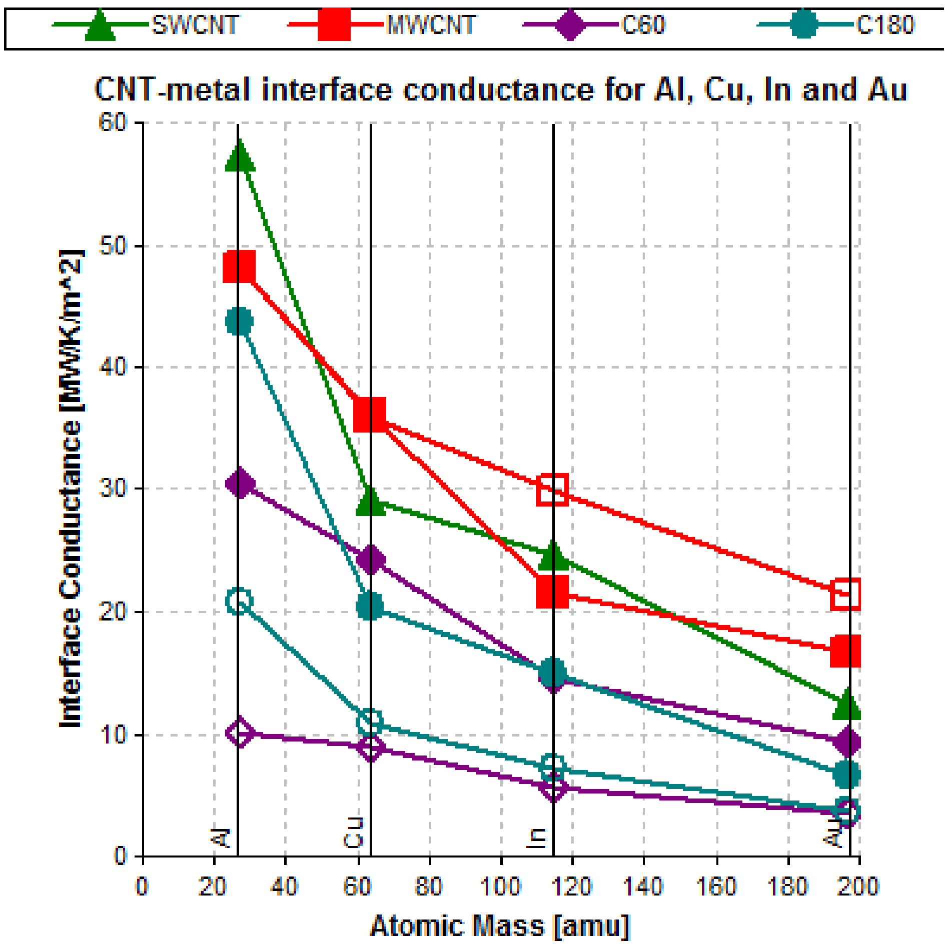


•No (or narrow) overlap in fullerene / metal vibrational spectra



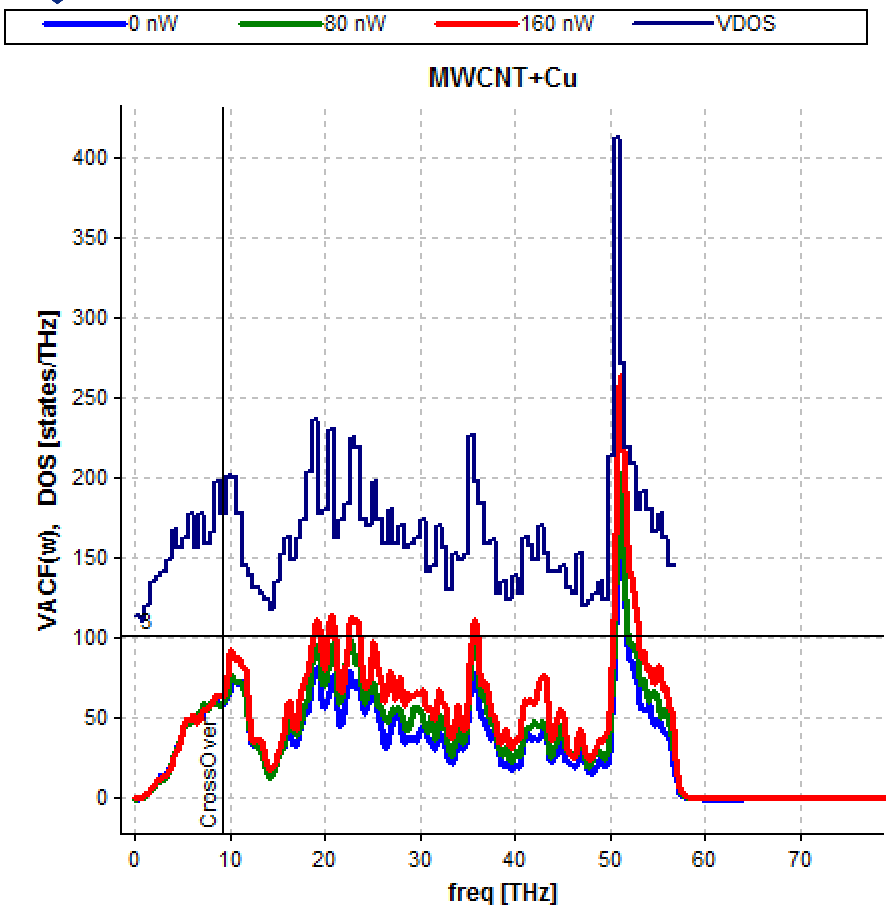


Conductance for Different Carbon-Metal Interfaces in NEMD Simulations



- **Values are low (metal-metal 300-1000 MW/m²/K)**
- **Similar conductance found for MWCNT and SWCNT interfaces**
- **Conductance is higher for lighter metal**
- **CNT interfaces show similar conductance in active heating and temperature relaxation modes**
- **Lowest conductance is for C_{60}/Gold interface in temperature relaxation mode (~3.5 MW/m²/K**
- **C_{60}/polymer without coating ~12..15 MW/m²/K)**

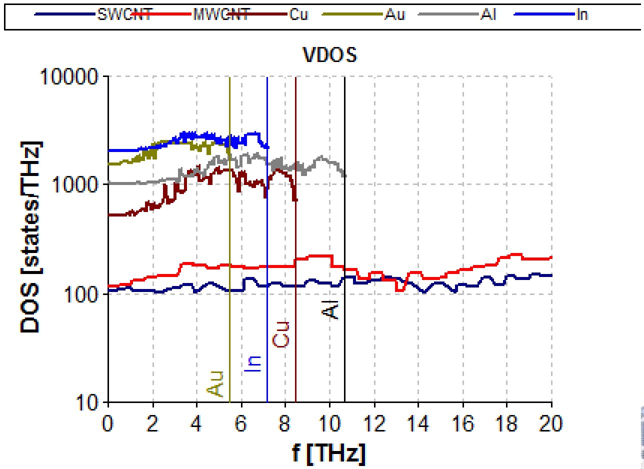
Energy of vibrational modes in NEMD – MWCNT in Cu



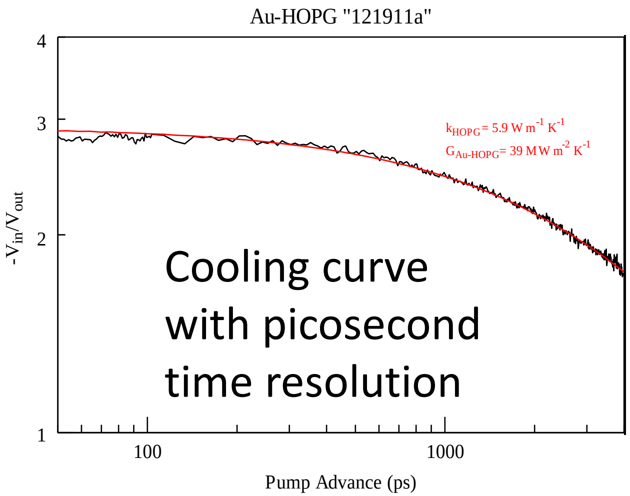
- The peeks of F(w) correspond to VDOS obtained from the vibrational analysis
- There is a sharp transition near Debye frequency of copper (~8.5 THz): vibrational modes at lower frequencies are "cold"
- Interfacial conductance is proportional to the "overlap" between VDOS of metal and CNT – diffuse mismatch model works

$$C(t) = \langle \vec{v}(t) \cdot \vec{v}(0) \rangle$$

$$F(\omega) = \frac{1}{2\pi} \int_0^\infty C(t) e^{-i\omega t} dt$$

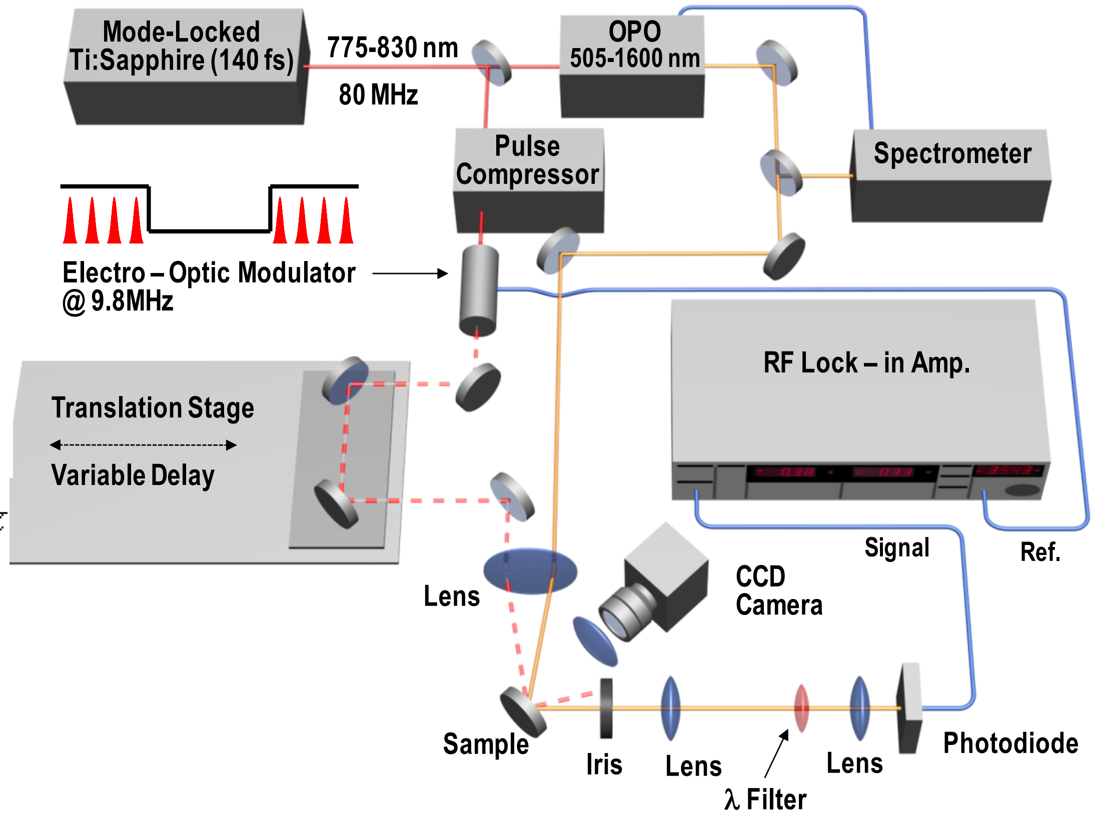


Interface Conductance Measurements with Time Domain Thermal Reflectance (TDTR)



Cooling curve with picosecond time resolution

TDTR schematic



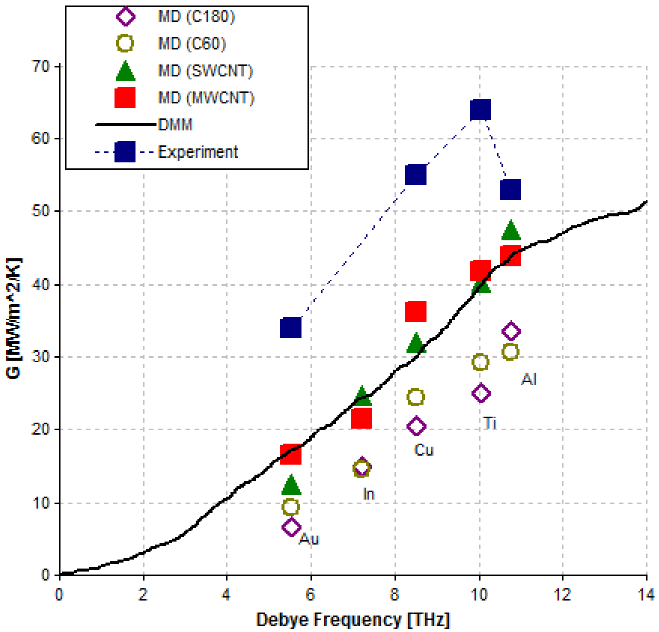
$$-\frac{V_{in}}{V_{out}} = \frac{\sum_{-m}^{m}\left(\Delta T(m/\tau+f)+\Delta T(m/\tau-f)\right)\exp(i2\pi m t/\tau)}{i\sum_{-m}^{m}\left(\Delta T(m/\tau+f)-\Delta T(m/\tau-f)\right)\exp(i2\pi m t/\tau)}$$

$$\Delta T = 2\pi A\int_0^\infty G(k)\exp\left(-\pi^2k^2(w_0^2+w_1^2)/2\right)\,k\,dk$$

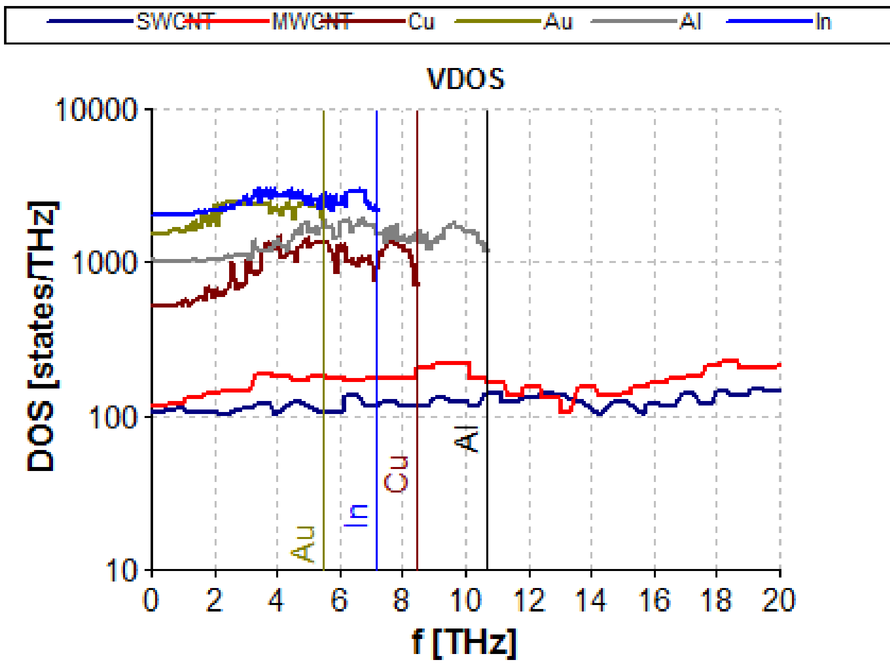
Undoubtedly the best technique for measurement of interface conductance, but requires R_a <25 nm!

(No way for nanotube-based materials!)

MD conductance for graphite-metal interface: well explained by DMM

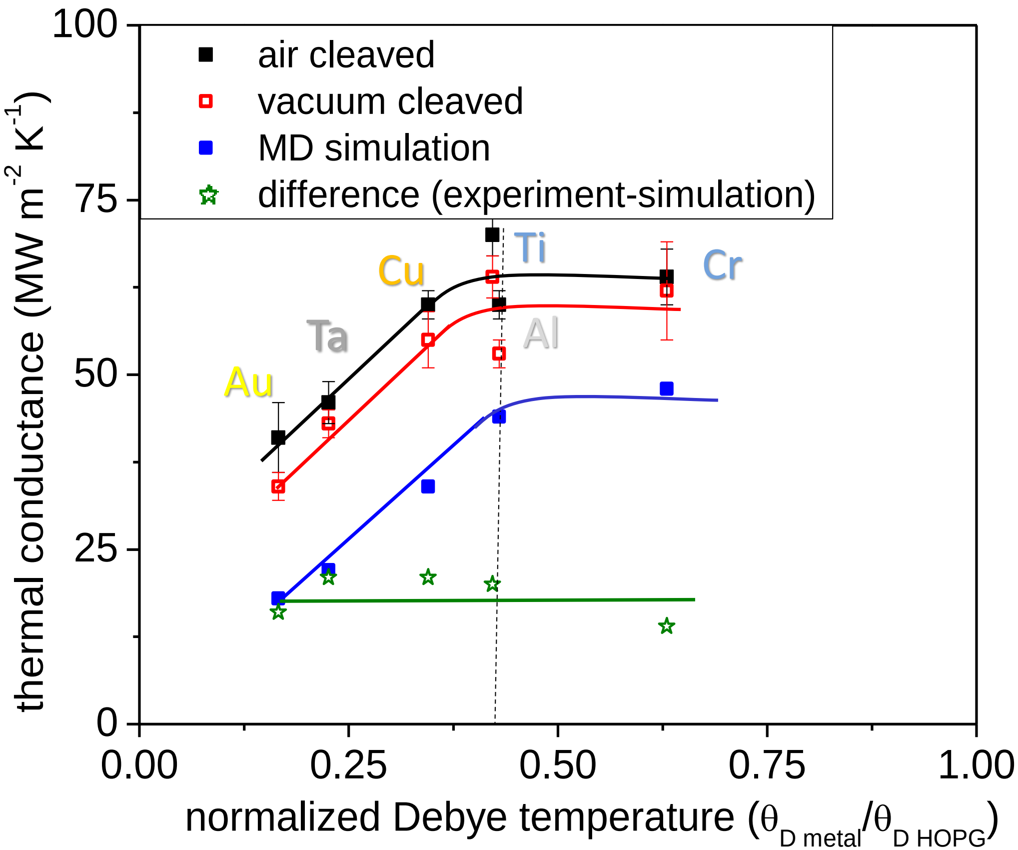


$$G = \int_{\omega} k_B \chi(\omega)\, \Phi_1(\omega)\Phi_2(\omega)\, d\omega$$



- **Conductance scales with Debye temperature of the metal (diffuse mismatch model works well)**
- **The constant is good approximation for spectral interfacial conductance for all studied metal-carbon interfaces**

Interface Conductance for HOPG and Different Metals



Observations:

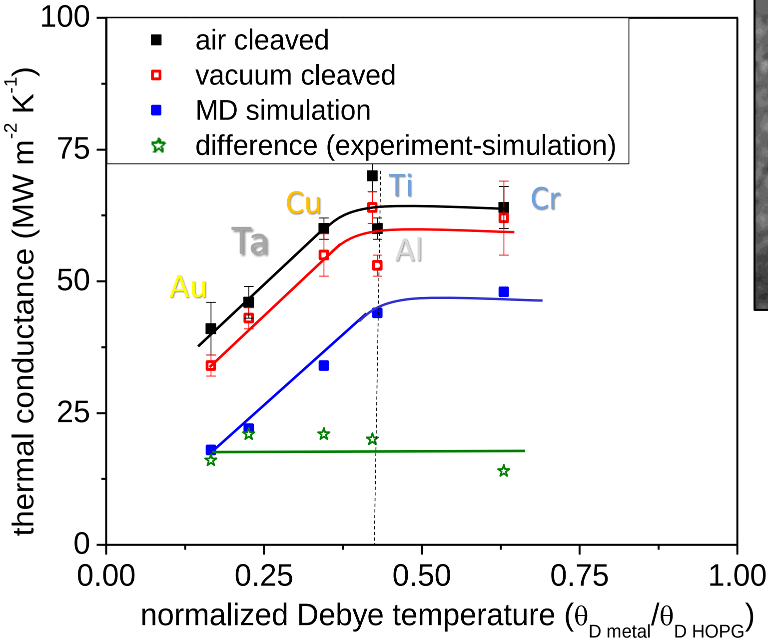
-Strong dependence on metal for $\theta_{D\ metal}$ <400K (~3x)

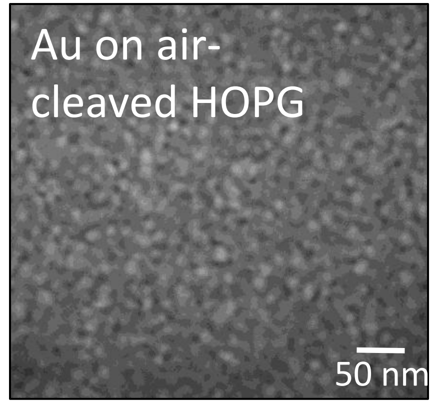
-Conductance levels off above ~0.5 ($\theta_{D\ metal}$ ~400 K)

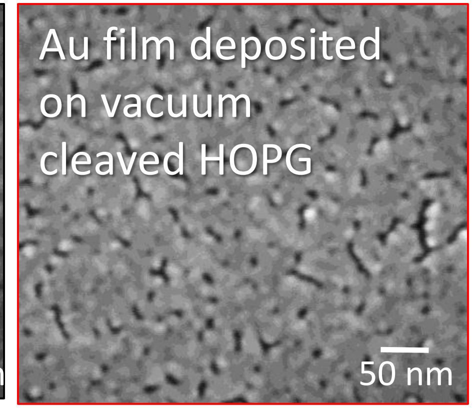
-Conductance for vacuum cleaved HOPG less than air cleaved (within error bars, but repeatable)

Effects of Vacuum Cleaving on Metal Morphology

≈15% reduction in *G* for vacuum cleaved HOPG







>15% reduction in interfacial contact area

Lagally, et al. Nature, 417 (2002) 902

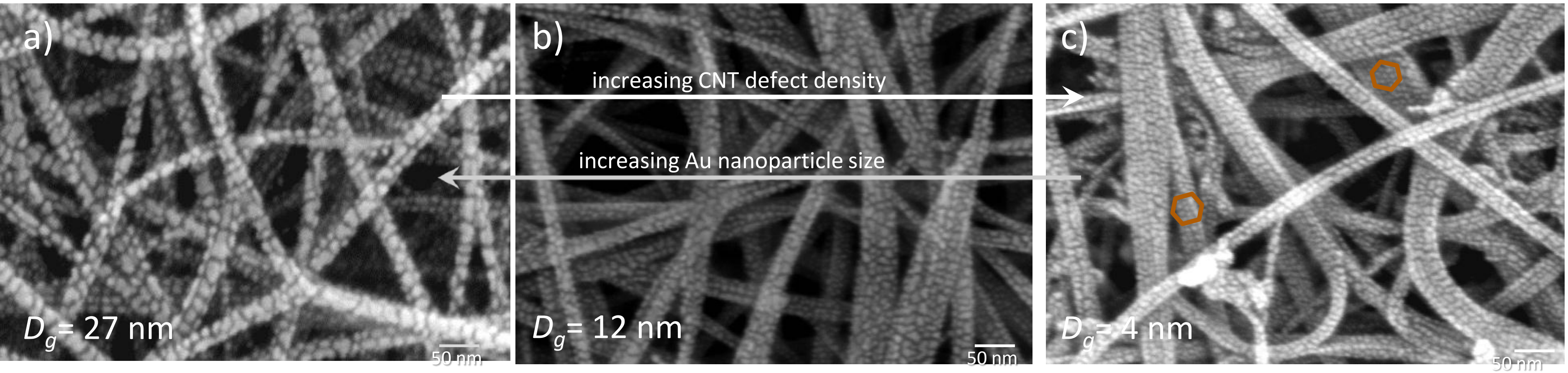
island corner barrier

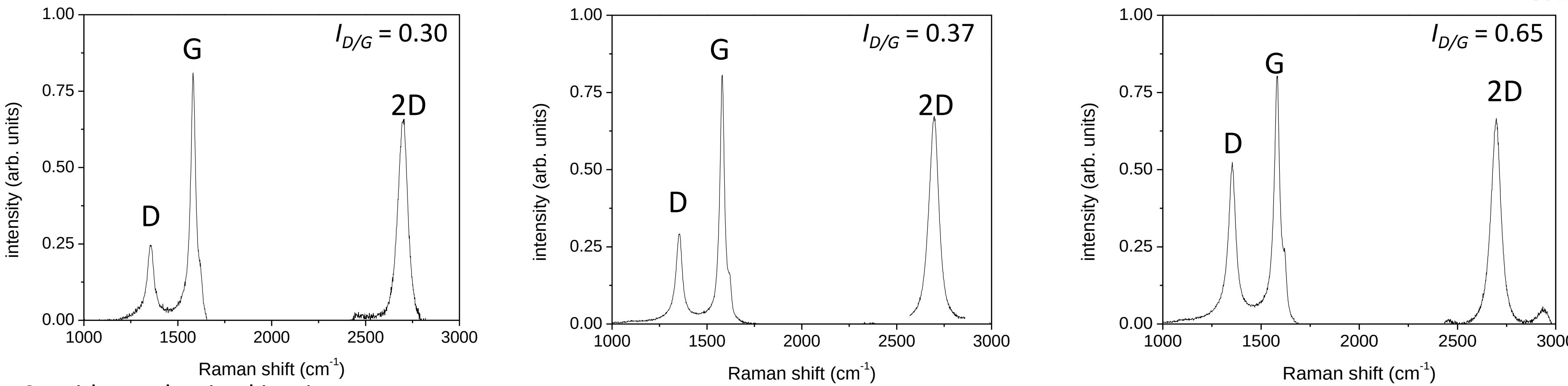
step barrier

Higher metal diffusivity on clean HOPG than on metal aggregates due to ES barriers

Same phenomena drives growth of ice dendrites on clean glass

Controlling Particle Size by Introducing Defects in-situ





Consider nucleation kinetics

$$\Delta G(j) = -j\Delta\mu + j^{2/3}X \quad \text{where,}$$

$$X = \sum_k C_k \gamma_k + C_{AB}(\gamma^* - \gamma_B)$$

γ^* = interface energy
γ_B substrate surface energy
C_k constant describing surface area island face
C_{AB} constant describing surface area film/substate

Differentiate ΔG to find critical size (at maximum)

$$i = \left(\frac{2X}{3\Delta\mu}\right)^3$$

Decreasing *X* by introducing defects decreases critical cluster size

Approved for public release: Distribution A (Case # 88ABW-2010-2822)

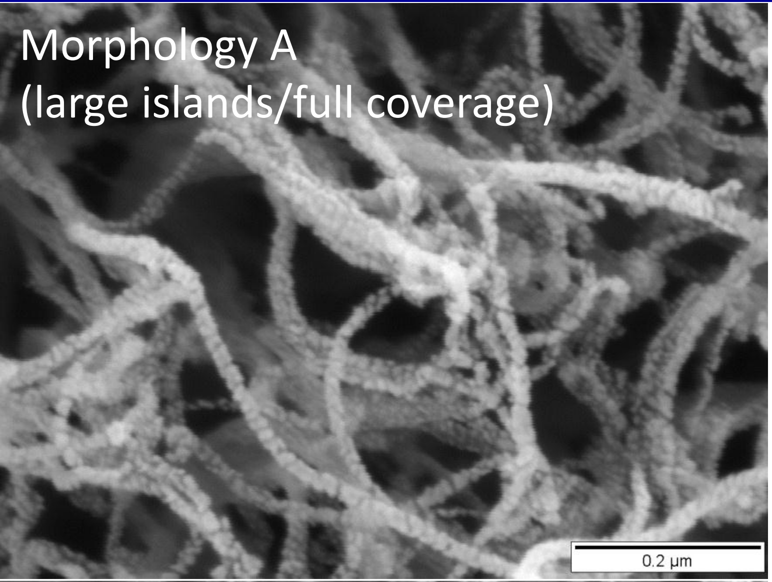
Kern, *Curr. Top. Mat. Sci.* **3** (1979) 139

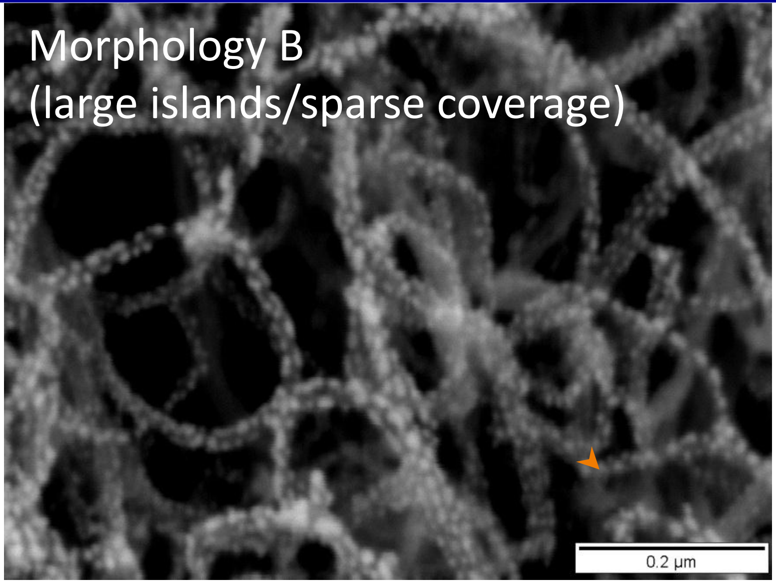
	Tensile strength	Thermal conductivity	Electrical conductivity
Carbon fiber (IM8)	6.1 Gpa	500 W m^{-1} K^{-1} at 22 °C	1 x 10^{3} S cm^{-1} at 22 °C
CNT yarn SOTA	3.5 GPa	60 W m^{-1} K^{-1} at 22 °C	2 x 10^{4} S cm^{-1} at 22 °C
Proposed target	10 GPa	500 W m^{-1} K^{-1} at 22 °C	4 x 10^{4} S cm^{-1} at 22 °C
Individual SWCNT	100GPa	3000 W m^{-1} K^{-1} at 22 °C	7 x 10^{4} S cm^{-1} at 22 °C

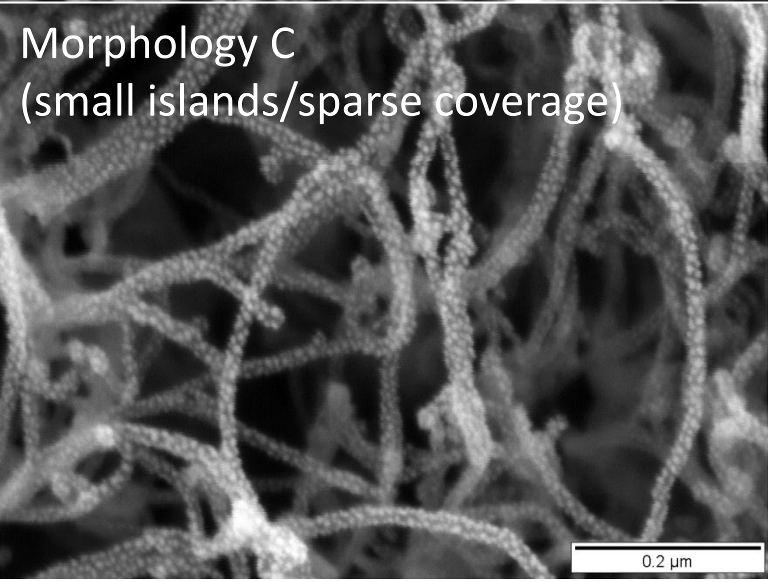
Copper σ—6 x 10^{5} S cm^{-1}

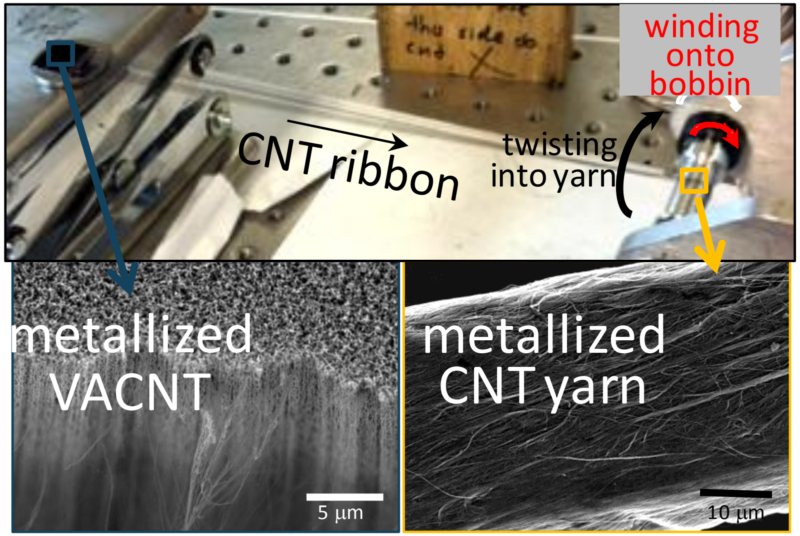
CNT yarn demonstrates comparable properties to state of the art carbon fibers, however, is still far away from single nanotube values

Investigating Effects of Morphology on CNT Yarn Properties

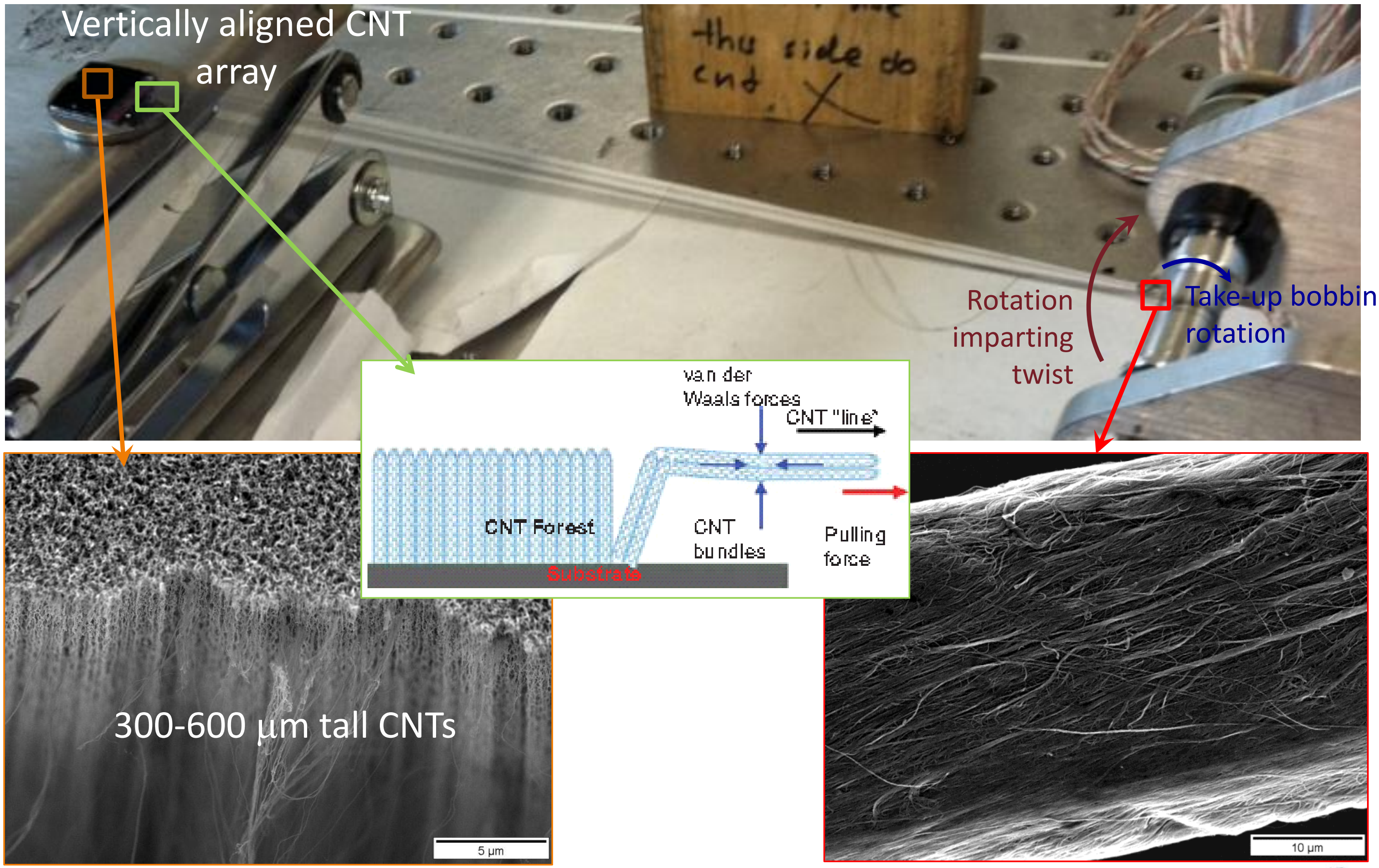








Dry Spinning of CNT Arrays into Carbon Nanotube Fibers



Correlation between particle size and melting point in literature

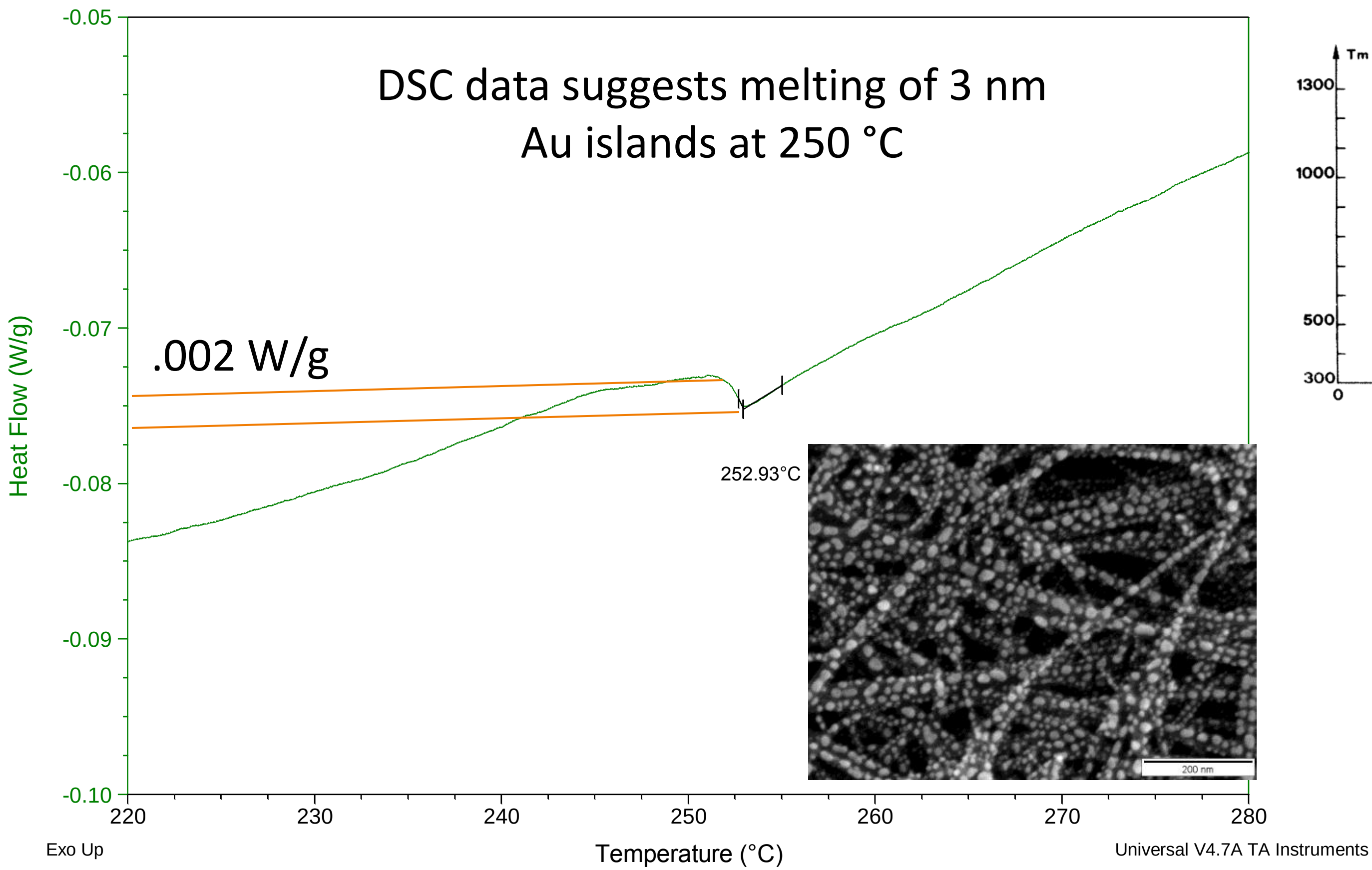
- **The relationship between the melting point of bulk material and a particle is given by,** ★

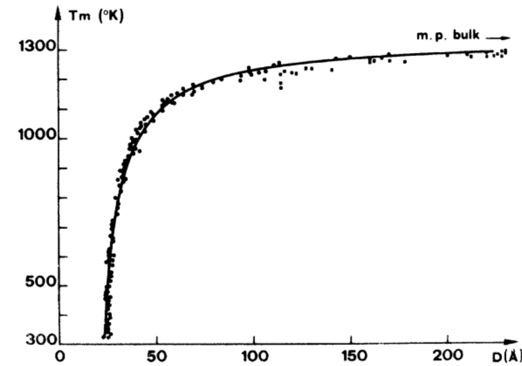
$$T_b - T_m = \left[\frac{2T_b}{\Delta H \rho_s r}\right]\left[\gamma_s - \gamma_l \left(\frac{\rho_s}{\rho_l}\right)^{2/3}\right]$$

where, T_b = melting point of particle, T_m = melting point of particle, r = radius of particle, ΔH = molar latent heat of fusion, γ and ρ = surface energy and density.

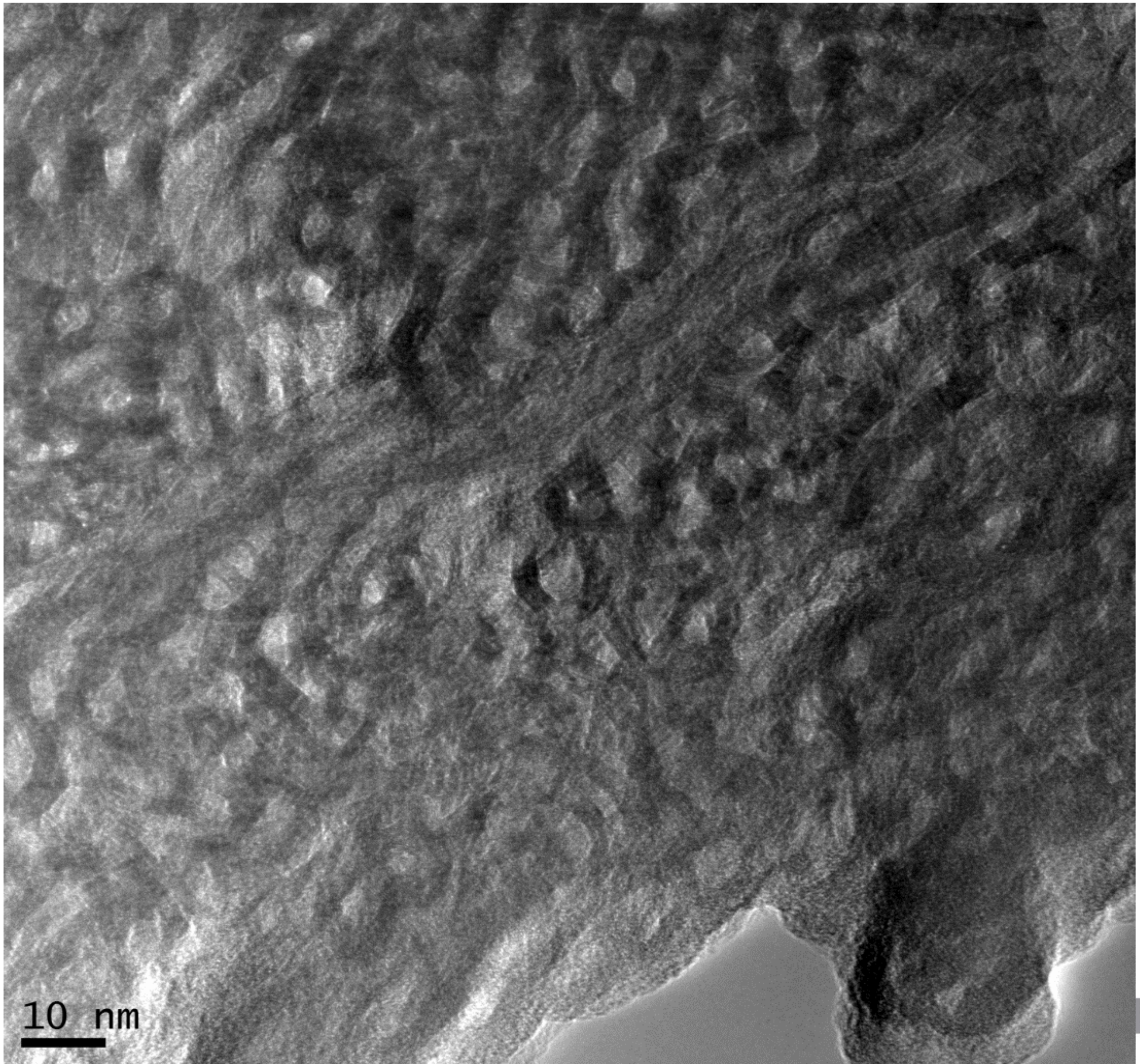
Buffat P, Borel JP (1976) Size effect on the melting temperature of gold particles. Physical Review A 13 (6):2287-2298*

Particles with Tailorable Melting Points

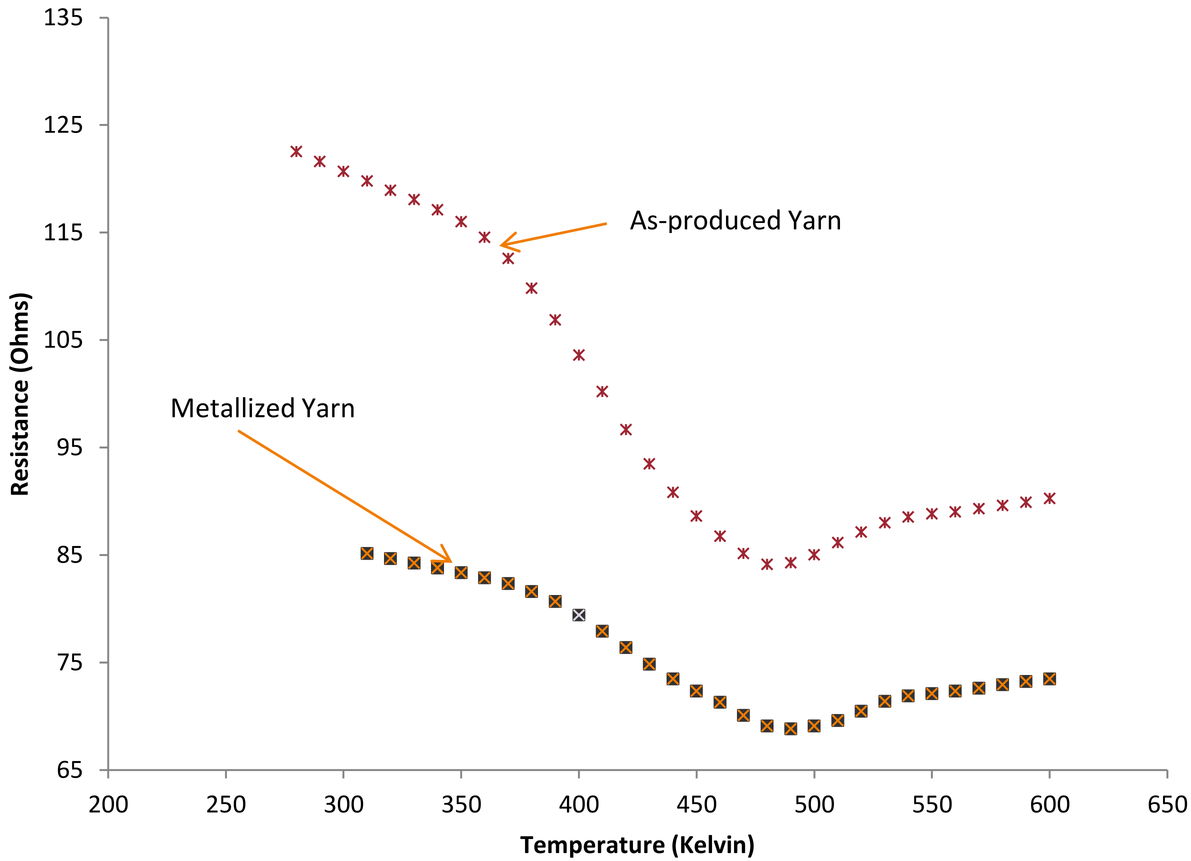




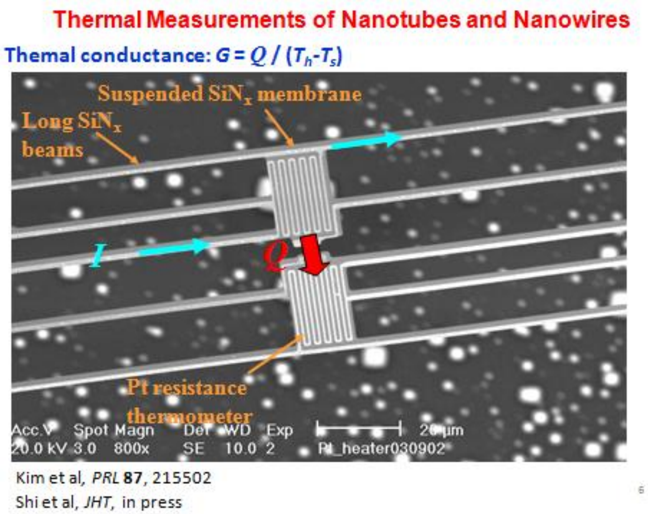
High Resolution TEM Micrographs of NT Yarn Cross-section



Electrical Properties of CNT Yarn by 4 Wire Probe

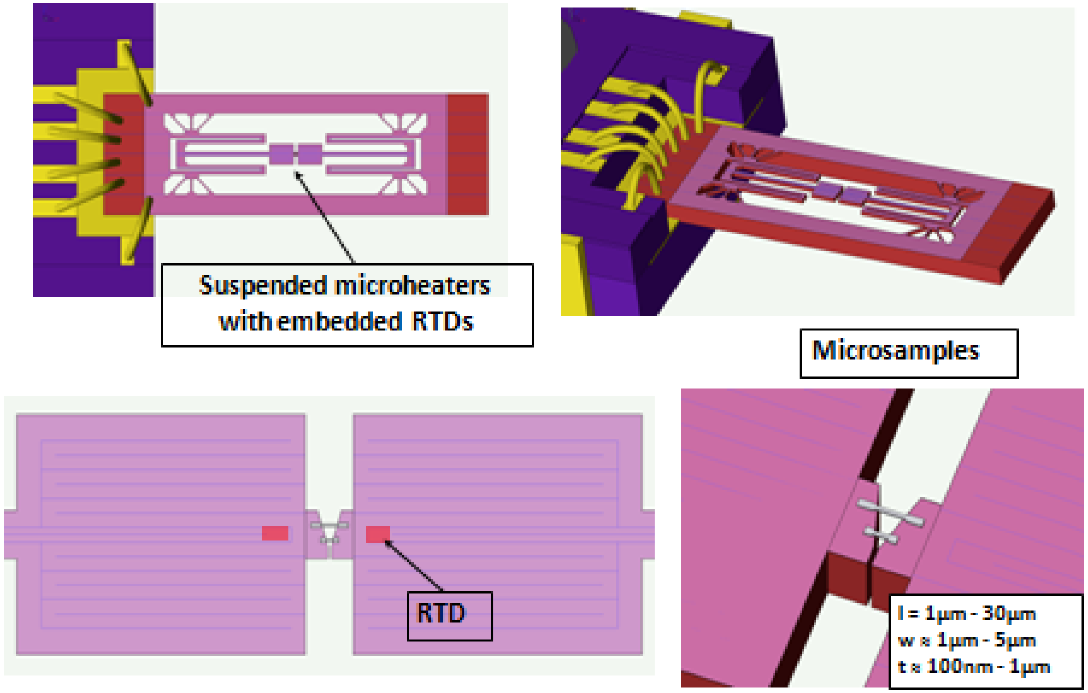


Microscale Thermo-Mechanical Measurements

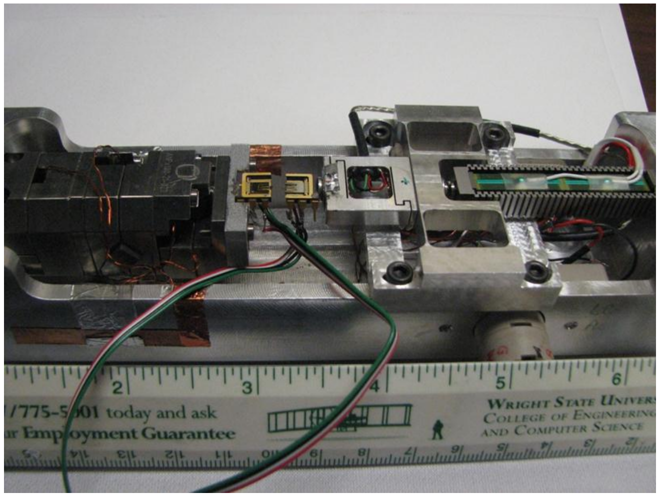


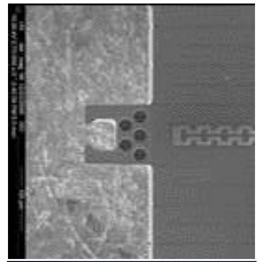
Kim et al, *PRL* **87**, 215502
Shi et al, *JHT*, in press

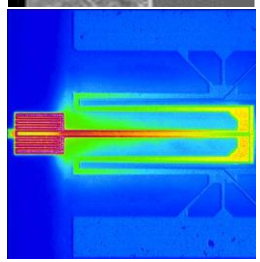
In-Situ Thermal Conductivity Experiment using AFRL/MCF Device

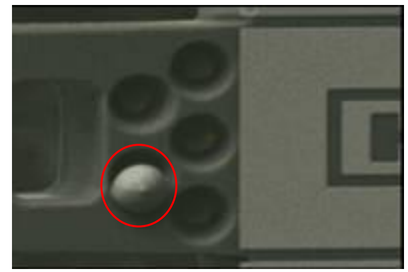


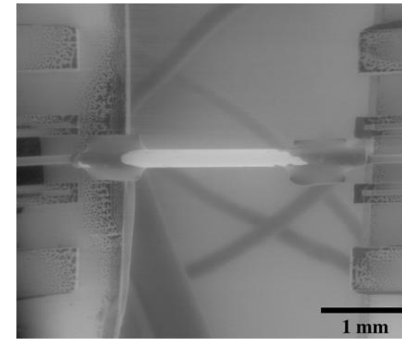
Temperature Calibration of the System & K Measurement of Standard Metal Wires

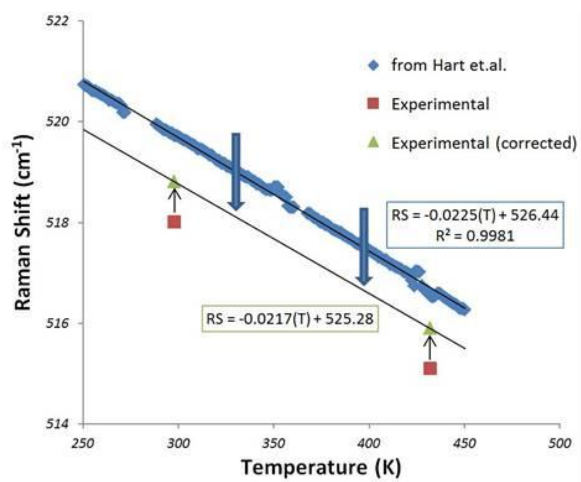


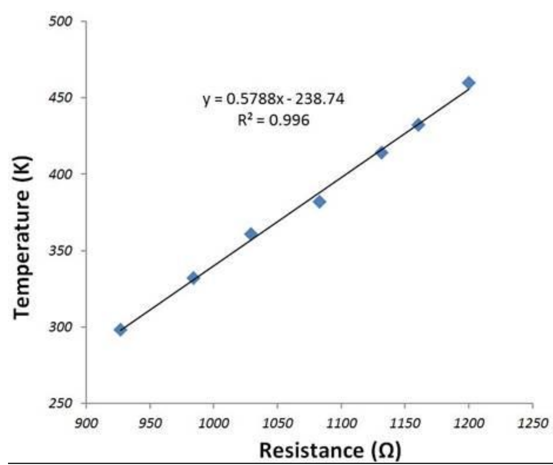


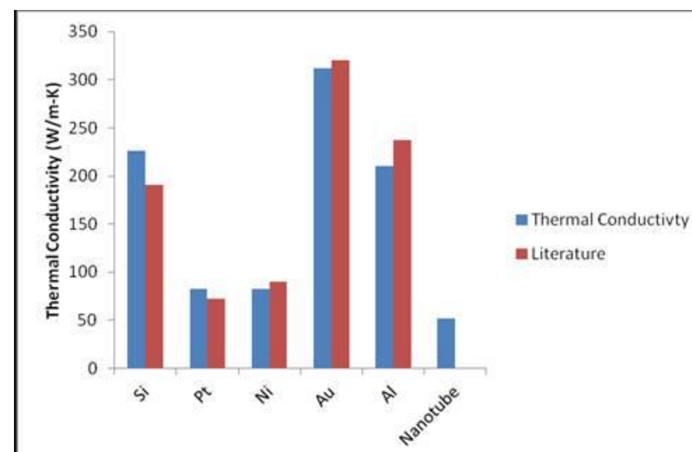




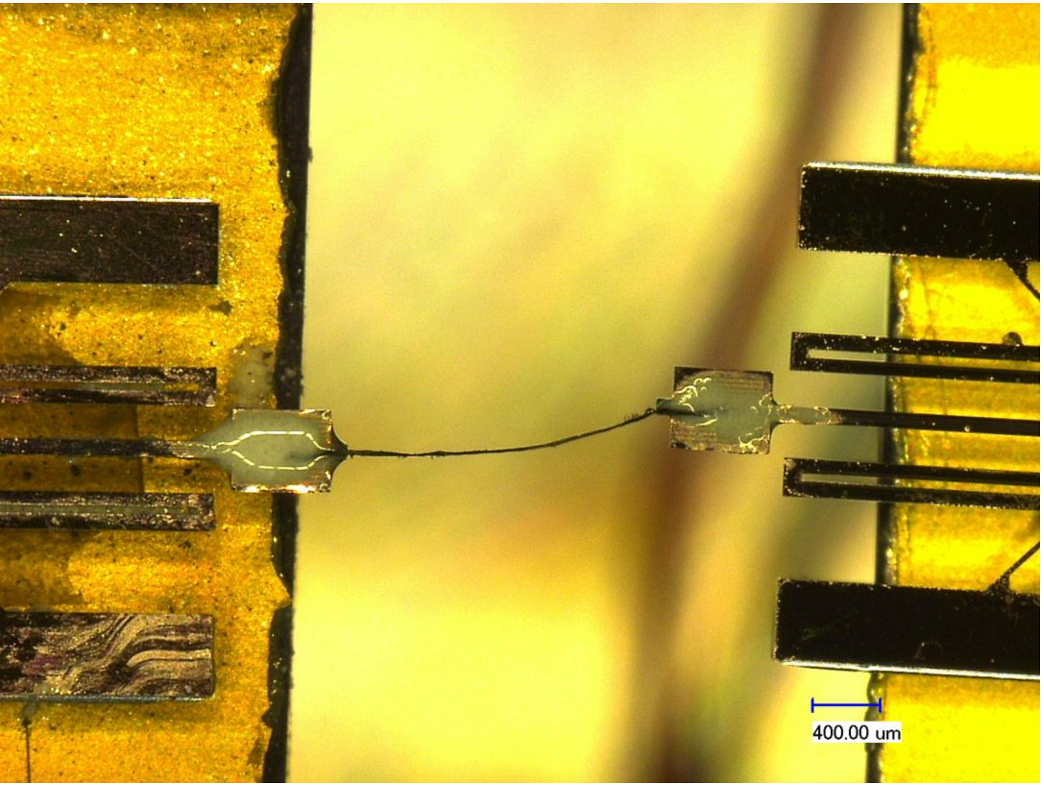






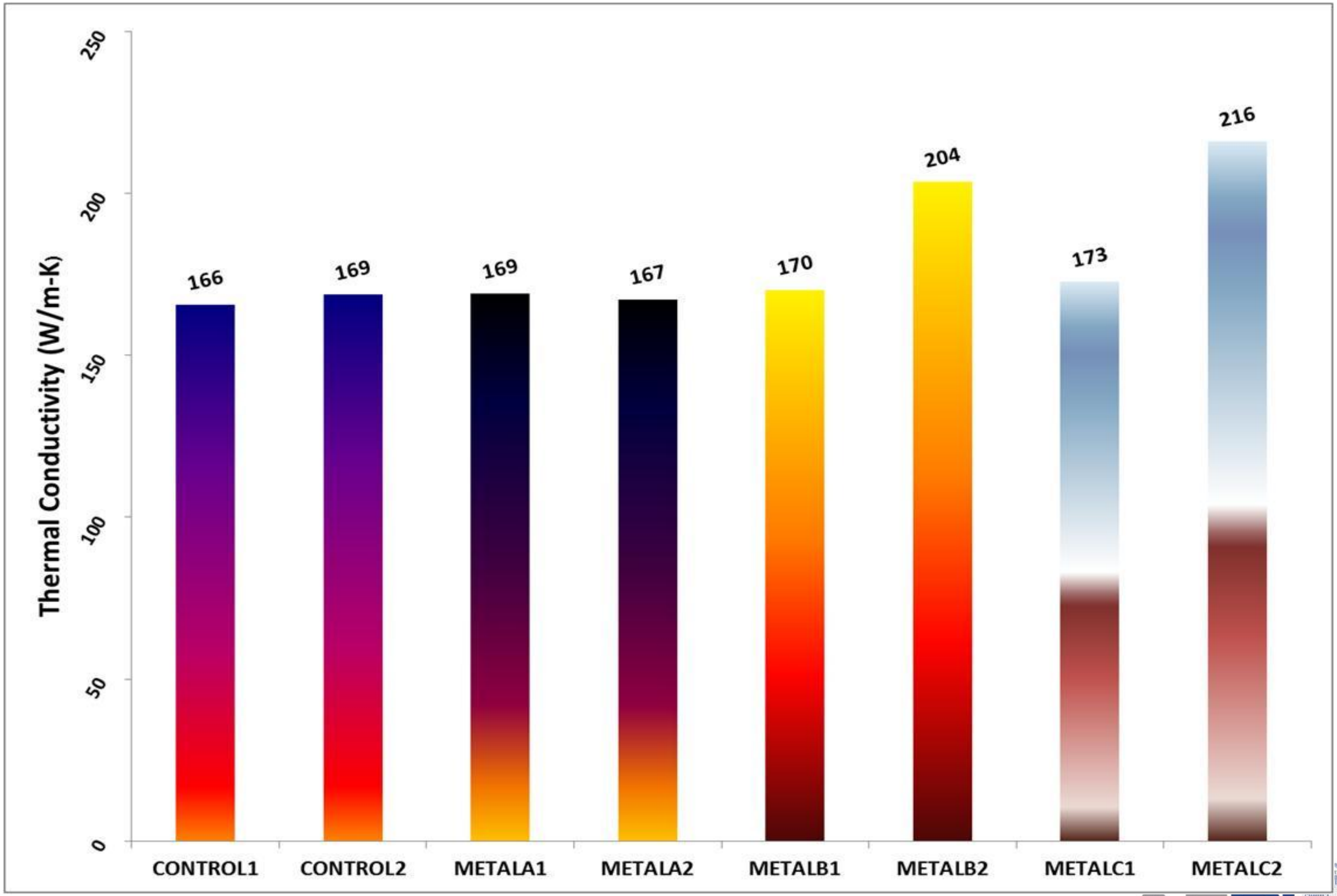


Thermal Conductivity Measurement Testing Protocol

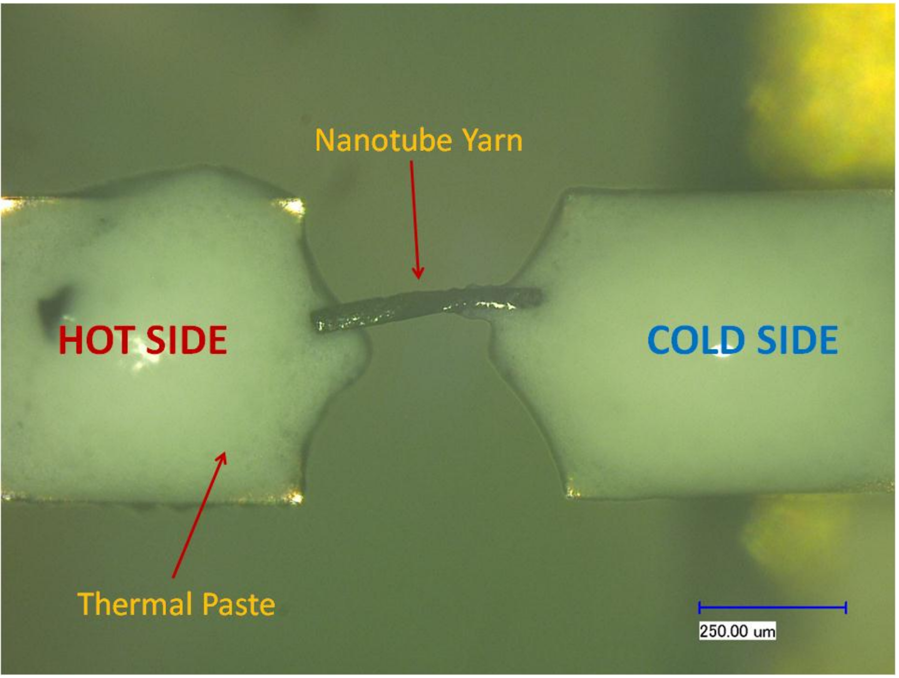


- *k* for each sample measured 3 times
  - First at RT
  - Annealed at 300 ^{o}C & cooled to RT
  - Repeat measurement at RT
- Omega® thermal grease used at the interface
- All measurements performed in a vacuum chamber
- Length and cross sectional area measured by EM

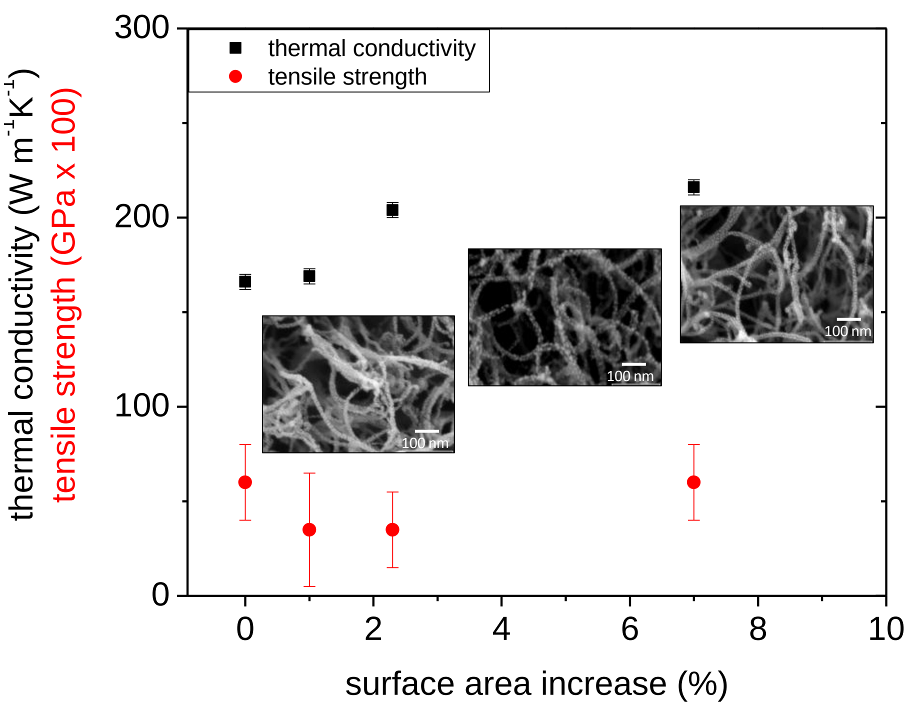
Measured Thermal Conductivity



Micro-scale thermal conductivity and mechanical property measurements

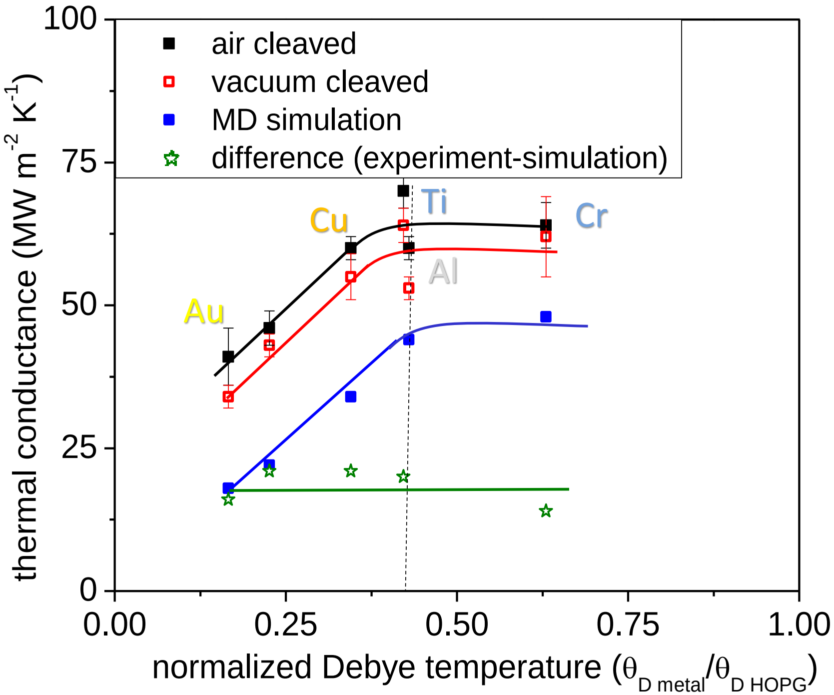


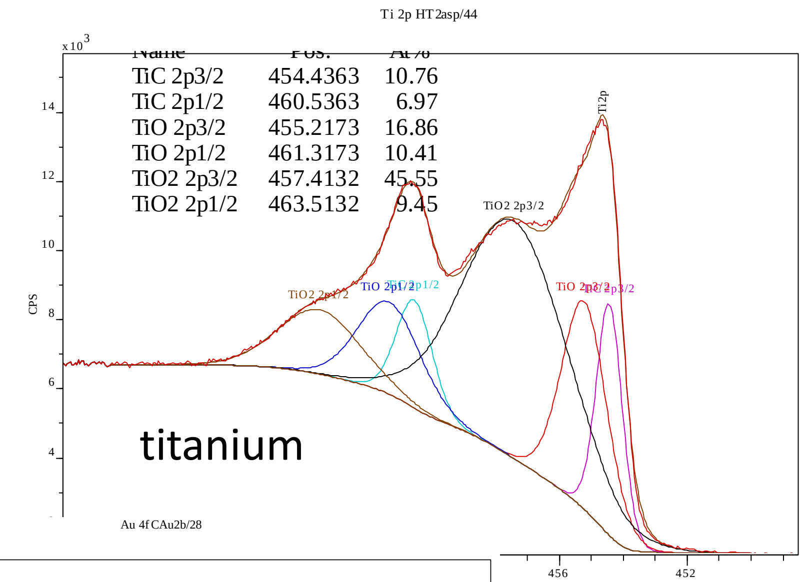
Metallization and annealing result in 30% increase in thermal conductivity without compromising mechanical strength

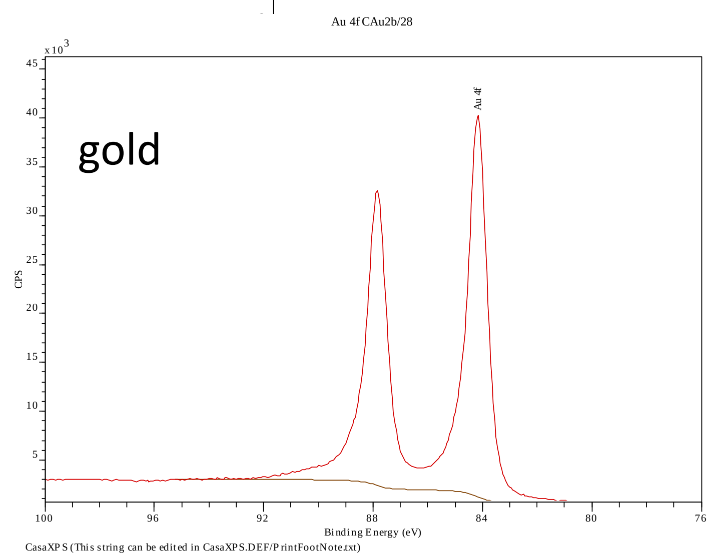


Materials Selection: Intrinsic vs. Extrinsic Effects on Conductance

Gold has lowest intrinsic conductance, however highest oxidation resistance

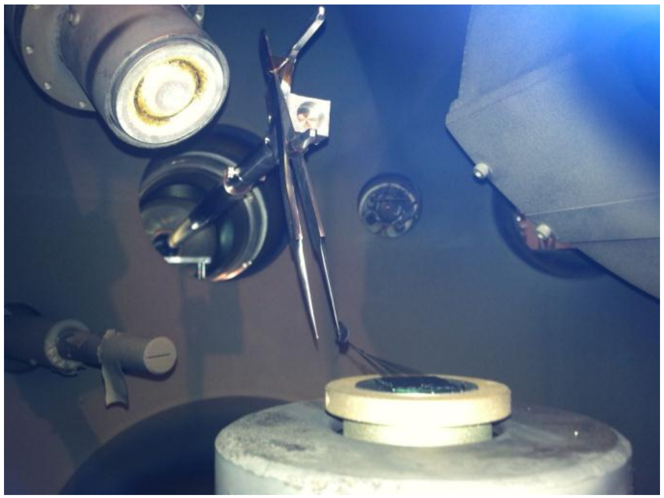


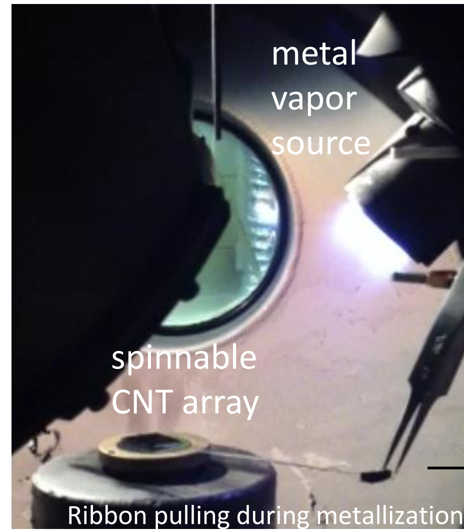




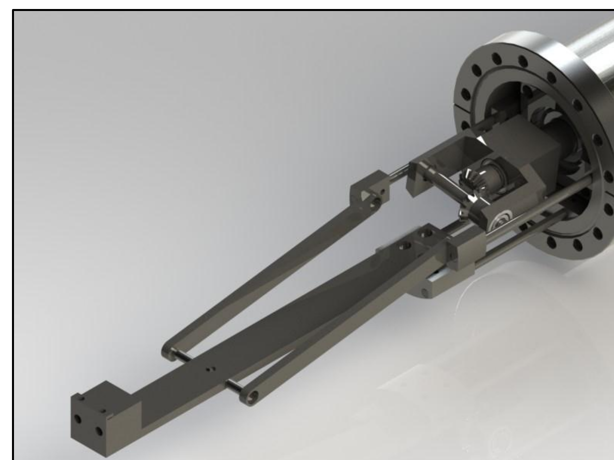
Overcoming Difficulties with non-gold Metallization within Vacuo Spinning

metallizing while spinning

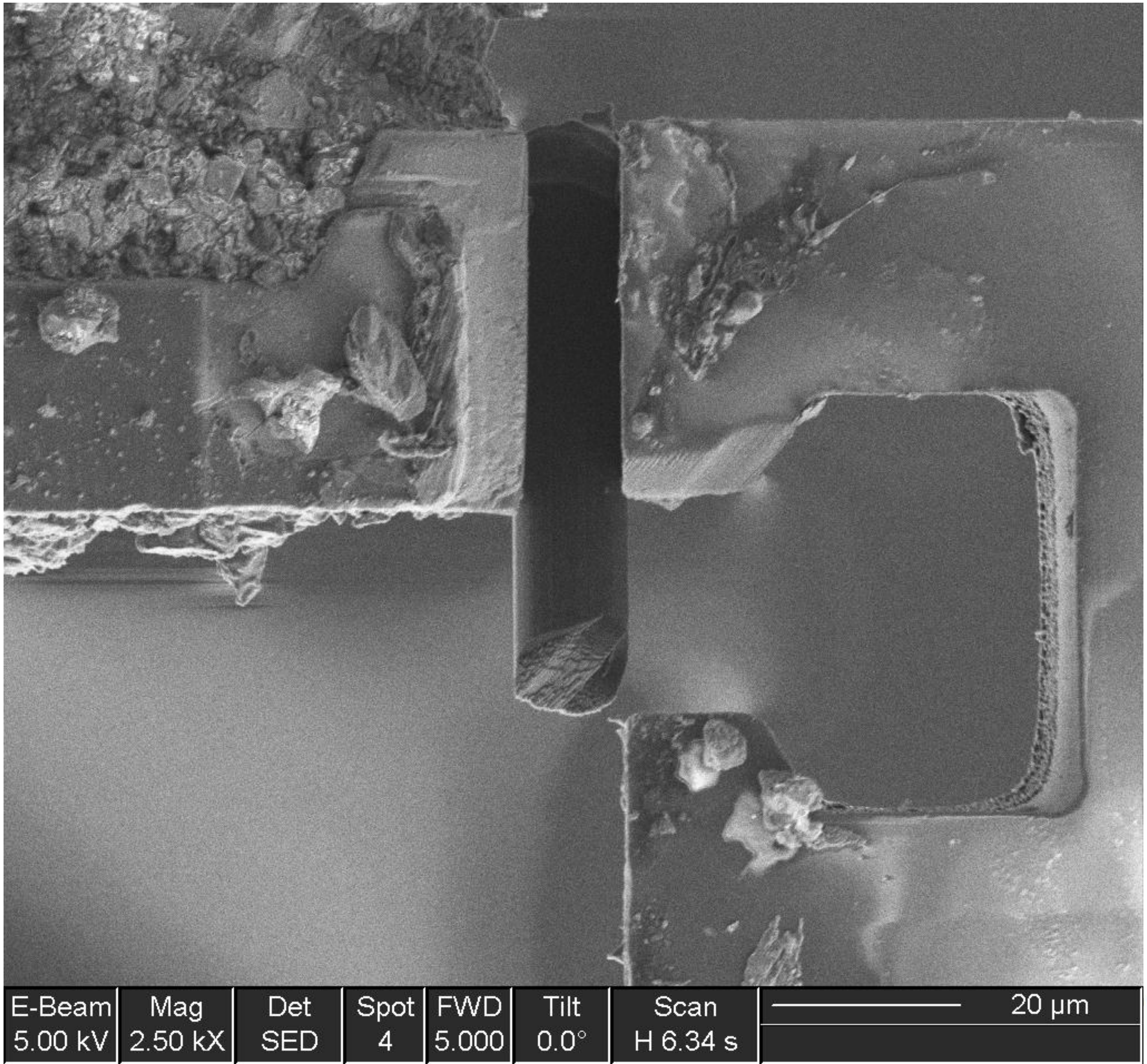




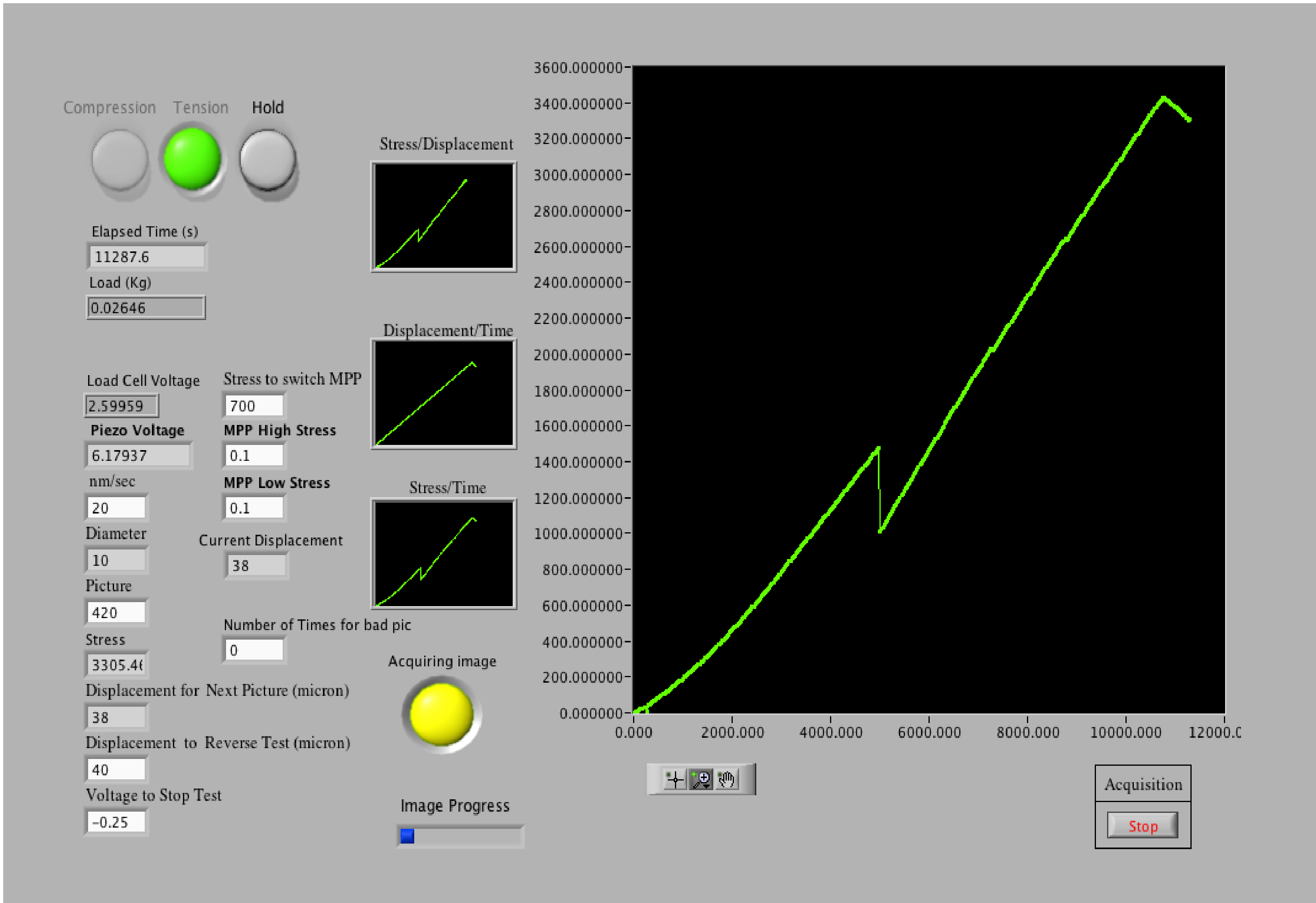
in situ spinning and annealing during UHV metallzation to avoid oxidation at critical interfaces affecting transport



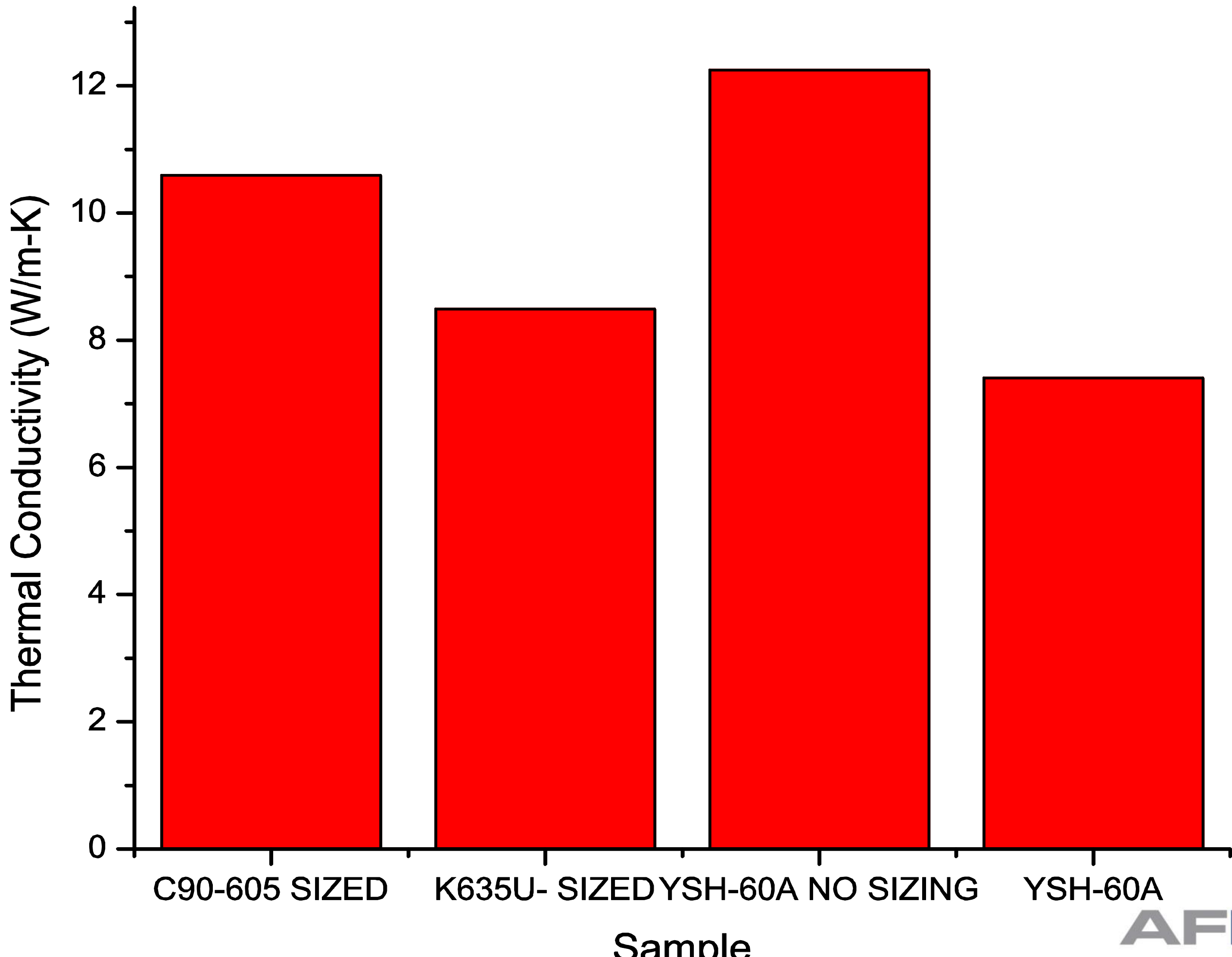
Direct Concurrent Thermal and Mechanical Property Measurement of Single Carbon Fiber



Load Displacement Measurement of Single Carbon Fiber Diameter ~ 12 µm



Transverse Thermal Conductivity of Pitch Carbon Fibers

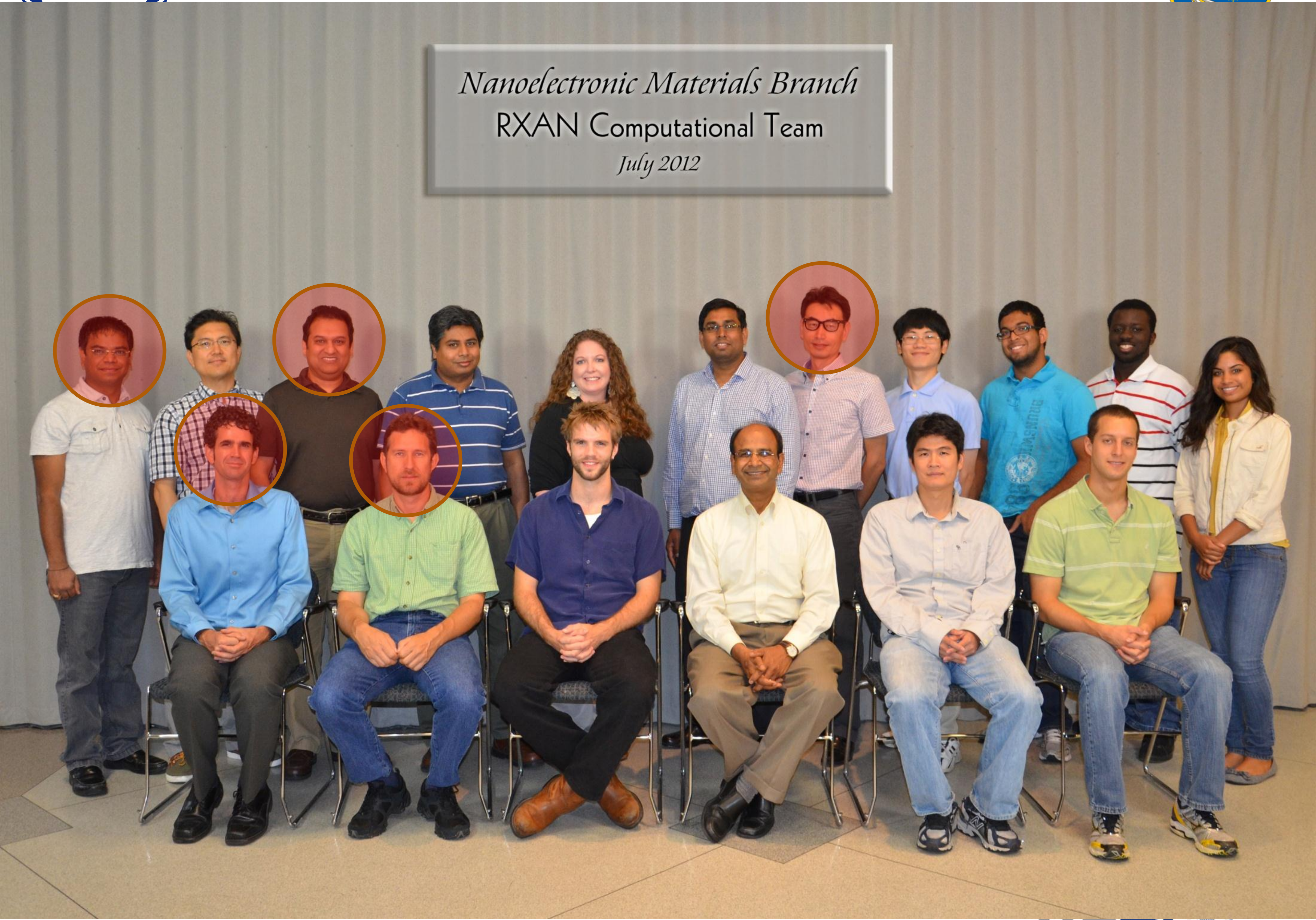


Summary

- **Metal-CNT interface thermal conductance – two dominant phenomena**
  - Electronic heating
  - Lattice vibration (phonon contribution)

- **Debye temp matching is extremely important for tailoring interface conductance**

- **Submicron scale combined thermo-mechanical property measurement capability**


Nanoelectronic Materials Branch
RXAN Computational Team
July 2012